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The Pennsylvania State University

The Graduate School

Department of Civil Engineering

**AEROBIC TREATABILITY OF WASTE
EFFLUENT FROM THE LEATHER FINISHING
INDUSTRY**

A Thesis in

Environmental Engineering

by

Jeffery A. Vinger

**Submitted in Partial Fulfillment
of the Requirements
for the Degree of**

Master of Science

December 1993

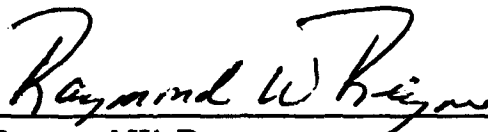
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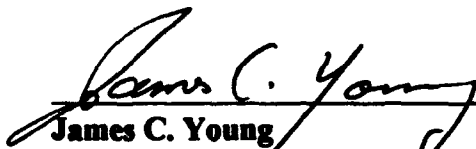
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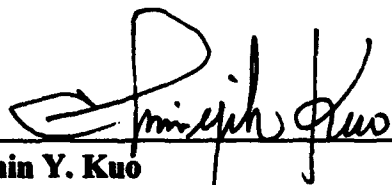
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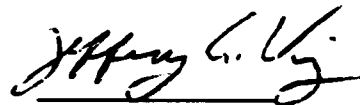
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Jeffery A. Vinger

Abstract

The Seton Company supplies finished leather products exclusively for the automotive industry. In the process of finishing leather, two types of wastewaters are generated. The majority of the wastewater is composed of water-based paint residuals while the remainder is composed of solvent-based coating residuals. Aerobic treatability studies were conducted using water-based and solvent-based waste recirculatory waters from the Seton Company's Saxton, Pennsylvania processing plant. The specific objective was to determine the potential for using aerobic biological processes to biodegrade the industry's wastes and determine the potential for joint treatment at the local publicly owned treatment works (POTW).

This study was accomplished in two phases. Phase I was conducted during the Spring Semester 1993 and consisted of aerobic respirometer tests of the raw wastes and mass balance analysis. The results of Phase I were published in a report to the Seton Company as Environmental Resources Research Institute project number 92C.II40R-1. Phase II was conducted during the Summer Semester 1993 and consisted of bench-scale reactor tests and additional aerobic respirometer tests. The aerobic respirometer batch tests and bench-scale reactor tests were used to assess the treatability of solvent-based and water-based wastewaters and determine the degree of biodegradability of the wastewaters. Mass balance calculations were made using measured characteristics. With the results obtained from aerobic respirometer tests, bench-scale tests and mass balance calculations, an assessment was made on the impact of the Seton Company's discharge on the POTW.

Phase I findings indicated that although there will be limited impact on the POTW hydraulically, there will be a significant increase in biochemical oxygen demand (BOD) loading imparted by the Seton Company's wastewater that would require the POTW to operate at 105% of its BOD load design capacity under current Seton Company

Abstract

operations and up to 151% of its design capacity under proposed expanded Seton Company operations. From the analysis results, direct discharge of all Seton Company's wastewaters without pretreatment is not a viable option. As will be presented, aerobic respirometer tests indicated that all of the wastewater samples taken from the Seton Company's Saxton plant were aerobically biodegradable, but only to a limited extent. Biodegradability ranged from a high of 48 percent for the booth 3 (solvent-based coatings) wastewater to a low of only 7 percent in the holding tank water for the recirculated samples. Some inhibition to treatment was evidenced in some of the samples and a period of acclimation was noted in others for the microbial cultures used.

Findings made with bench-scale reactor tests in Phase II indicated there was some effect on the treatment systems even with the low loadings expected under the current Seton Company operations. Gas chromatography analysis of the effluents generated in the bench-scale reactor tests showed the presence of solvents indicating decreased or incomplete treatability. Aerobic respirometer tests of effluents generated by the bench-scale reactors indicated elevated BOD reaction rates in the parallel POTW operation sequence, but satisfactory BOD reaction rates in the series POTW operations sequence.

Overall, the use of aerobic biological processes as the sole means to biodegrade the leather finishing industry's effluent wastes and the potential for treatment at the local POTW were not recommended. Further investigation might be made on the advantages of anaerobic pretreatment of the wastewaters and effects of physical pretreatment or solvent recovery on improving the treatability of this source of industrial wastewater.

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Abbreviations

COD	Chemical Oxygen Demand
SCOD	Soluble COD
TCOD	Total COD
MCR	Master Culture Reactor
NMB	Nutrient/Mineral/Buffer Medium
SRT	Solids Retention Time
SS	Suspended Solids
TSS	Total Suspended Solids
VSS	Volatile Suspended Solids
MGD	Million Gallons per Day
BOD	Biochemical Oxygen Demand
TOC	Total Organic Carbon
TKN	Total Kjeldahl Nitrogen
NPDES	National Pollution Discharge Elimination System
POTW	Publicly Owned Treatment Works
RBC	Rotating Biological Contactor
MEK	Methyl Ethyl Ketone
MIBK	Methyl Isobutyl Ketone
TCA	Tricarboxylic Acid
TLV	Threshold Limit Value
BP	Boiling Point

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Introduction

1.1 Statement of Problem

The Seton Company is a leather finishing industry which currently operates with a dry process, meaning that no industrial wastewaters are discharged from the plant. The Saxton, Pennsylvania plant disposes of its process wastewaters through a contractor, on a batch basis. The Seton Company feels it would be mutually advantageous to both themselves and the Borough of Saxton if the wastewaters could be treated by the publicly owned treatment works (POTW). The problem needing resolution is whether the wastewaters will have an adverse effect on the wastewater treatment plant and whether the municipal plant has the capacity to treat the additional waste load.

1.2 Objectives

The general purpose of this project was to assess the impact on the local POTW if the Seton Company is allowed to discharge its wastewaters to that facility. The specific objectives of this project is to assess the treatability of the Seton Company's wastewaters in an aerobic environment and determine the effects of those wastewaters on the Saxton POTW. The laboratory investigation involved treatability studies using aerobic respirometer tests to assess biodegradability of wastewaters composed of water-based paint and solvent-based coating residuals, mass-balance analysis to determine the loadings to be expected in the waste flow to the POTW, and bench-scale reactor tests to determine the response of aerobic cultures to longer term feeding of the wastewater.

1.3 Overview

The Seton Company is located in the south-central Pennsylvania town of Saxton. The community of Saxton has a current population of 2150 people. The Seton Company is the only industry within a 30 mile range of Saxton. The Seton Company was founded in

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1898 as a supplier of horse and buggy leathers for the carriage trade. Today, the Seton Company continues its tradition as a supplier of leathers for seats and interiors exclusively for the automobile industry. As the Saxton plant deals only with the finishing of leather, it receives its "green" hides from tanneries throughout the United States. The tanned hides undergo a number of processes including conditioning, coloring, and sealing before they are finally cut to the shapes and sizes requested by Seton's customers. A brief summary of Seton's leather finishing operation and a description of Saxton's wastewater treatment plant is provided in the remainder of this section.

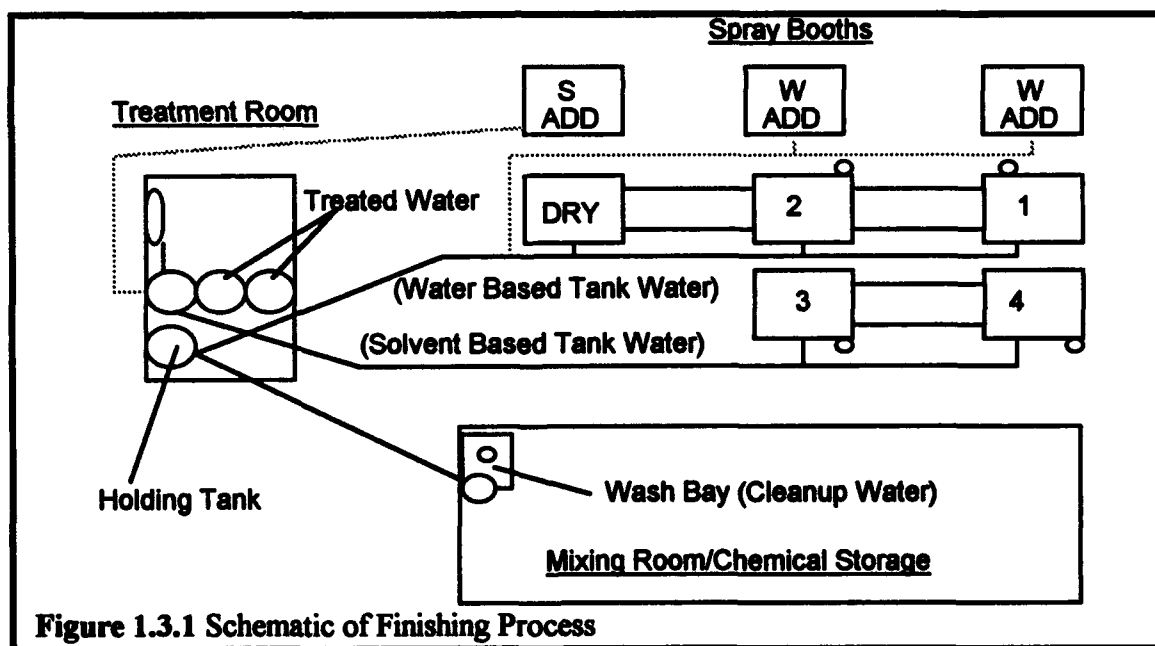
The conditioning process is a totally physical process of mechanical stretching and tumbling. The conditioning process softens the hides. As the conditioning process is a physical one, no wastewaters are generated.

After conditioning, the hides are subjected to a coloring and finishing process. Figure 1.3.1 is a schematic drawing of the coloring and finishing process. The process is an assembly line in which the hides are placed on a moving conveyor belt that travels the length of the warehouse facility in and out of various spray booths and dryers. The first booth sprays an even coat of water-based primer paint over the surface of the hide. The hide travels through a dryer to the second booth where it receives an even coat of a pigmented, water-based paint giving it its final color. The hide travels through another dryer to the third booth which sprays an even coat of solvent-based protectant over the painted hides providing a water-proof, abrasion resistant, and pliable seal to the surface. Each of the spray booths holds 1000 gallons of the recirculating water-based paint or solvent-based sealant. Four booths are currently in operation, but the company intends to expand the process with 3 more booths. These booths are the major source of generated

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wastewater. The water-based waste is pumped to a nearby fiberglass tank for storage. The solvent-based waste is pumped to another fiberglass tank for treatment.

A minor source of wastewater is the cleaning of tanks used in mixing of paints and solvents used in the spray booths. These 150 gallon stainless steel tanks are mixed in the chemical storage warehouse and wheeled into the assembly line area where they are connected to the sprayer systems. When empty, the tanks are wheeled back to the warehouse where they are cleaned with a high-pressure hose and detergent. The waste water generated in this cleaning operation varies on production schedules (color changes), but ranges from 250-500 gallons per day. The wastewater is combined with the water-based wastewater in the fiberglass storage tank.



The solvent-based wastewater in the storage tank is currently processed once a week. Alum is rapid mixed with the water as it is transferred to a cone tank. As the sludge settles, it is drawn off through a sludge press. The sludge cake produced by the press is placed into 55 gallon drums and stored. An average of four drums per week is

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produced. The drums are currently disposed of as hazardous waste at a cost of \$350 per drum. The "recycled" water drawn from the settled sludge in the cone and separated in the sludge press is pumped into a holding tank for use as makeup water in the solvent-based coating spray booth tanks. Approximately once a month, depending on production schedules, the water-based paint wastewater is transferred to a tank truck and disposed by a contractor.

After the hides are conditioned, colored, and finished they are cut by hand in patterns supplied by the Seton Company's customers, automobile manufacturers. There are no waste waters associated with this final process.

The overall desire of the Seton Company is to be able to dispose of all wastewaters through the sewage system avoiding the expense of disposal through a contractor. The Seton Company feels it would be mutually advantageous to both themselves and the Borough of Saxton if the wastewater could be treated by the POTW. Average flows to be expected from the Seton Company plant are listed in Table 1.3.1.

Existing Operations							
Water-based Effluent	Booth 1	Booth 2	Booth 4	Wash Bay			Total
	1000 gpd	1000 gpd	1000 gpd	500 gpd			3500 gpd
Solvent-based Effluent	Booth 3						
	1000 gpd						1000 gpd
							4500 gpd
Future Operations							
Water-based Effluent	Booth 1	Booth 2	Wash Bay	Booth 4	Booth 5	Booth 6	Total
	1000 gpd	1000 gpd	1000 gpd	1000 gpd	1000 gpd	1000 gpd	6000 gpd
Solvent-based Effluent	Booth 3	Booth 7					
	1000 gpd	1000 gpd					2000 gpd
							8000 gpd

Table 1.3.1 Expected Wastewater Flows

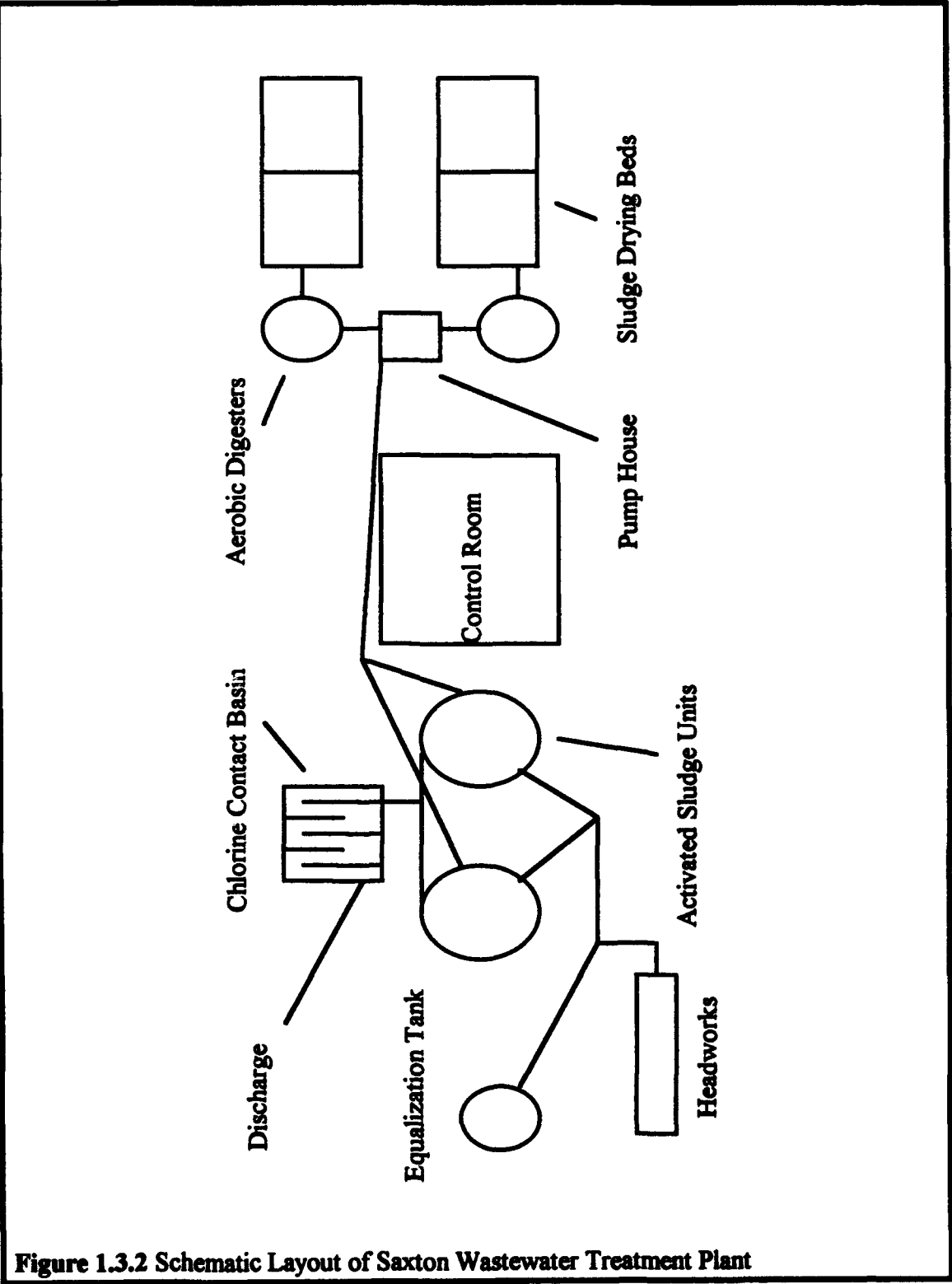


Figure 1.3.2 Schematic Layout of Saxton Wastewater Treatment Plant

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The POTW is located on the outskirts of the Borough of Saxton. Figure 1.3.2 is a schematic layout of the POTW. Very little space is available for any further expansion as the plant is situated on a hillside, surrounded by housing and further confined by a floodplain.

The wastewater produced by the Saxton community flows to a lift station approximately 300 yards from the treatment plant. Figure 1.3.3 gives a summary of the Saxton Wastewater Treatment Plant's annual flows and loading of biochemical oxygen demand, suspended solids, ammonia and phosphorus. The data for this graphical analysis was obtained from the POTW's discharge monitoring reports during the period of October 1991 through October 1992. The wastewater collected at the lift station is pumped to the treatment plant headworks which consists of an elevated, manually-cleaned screen and a Parshall flume for flow monitoring. The wastewater flows via gravity into one of two equalization tanks. The larger of the two is for incoming wastewater, while the smaller tank is used to store waters decanted from the activated sludge treatment units and aerobic sludge digester tanks. The wastewater from the equalization tanks is pumped into one of two circular activated sludge treatment units. These units operate in parallel. Liquid alum is added to the aerating wastewater to reduce phosphates. From these treatment units the water flows via gravity into a chlorine contact disinfection tank and then through a pipeline into a nearby stream and eventually into Raystown Lake. The sludge is pumped out of the activated sludge units and placed in one of two aerobic sludge digester tanks. After thickening, the water is decanted off into the smaller equalization tank mentioned earlier and the sludge drained out into one of two sludge drying beds. The Borough of Saxton is attempting to obtain a permit for land application of the sludge, but

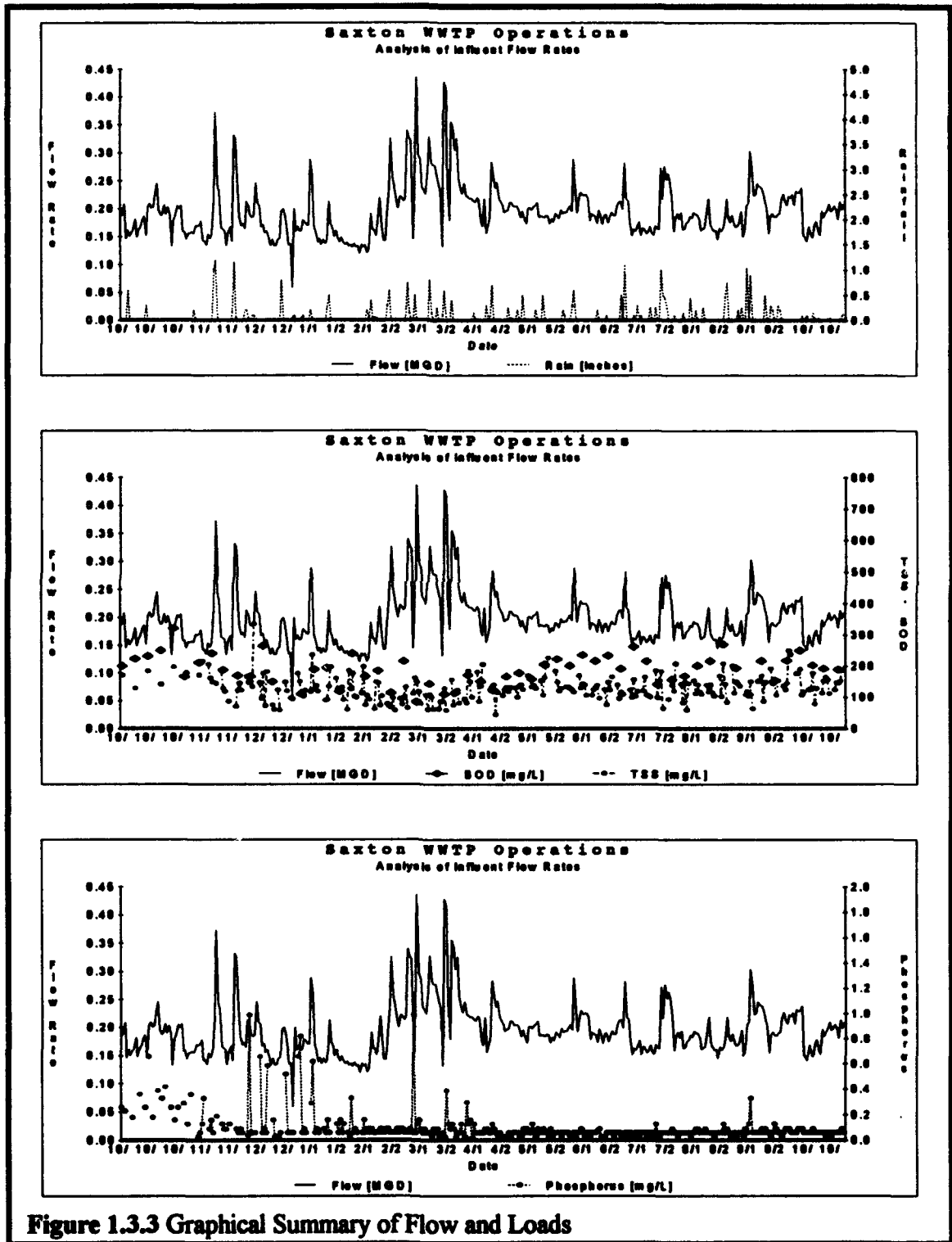
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as yet has been unable to locate and obtain approval for a suitable farm for the application. Until approval is given, the resultant sludge must be disposed of by landfilling.

1.4 Wastewater Characteristics

Table 1.4.1 lists characteristics of solvent-based coatings and water-based paint wastewaters that were tested in this project. Characteristic values were obtained from filelaboratory reports provided by the Seton Company. Laboratory analysis of listed samples was conducted 11 March 1992 by MDS Laboratories, Reading, PA. Some processes have changed since the date of the testing and the time of recirculation is unknown, so the values in Table 1.4.1 are provided only to demonstrate the chemical makeup typifying the Seton Company's wastewaters.

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Characteristic (mg/L, except as noted)	Solvent-based	Water-Based
pH (unitless)	6.99	6.50
BOD	529	526
TOC	6640	12025
Color (color units)	1000	25000
Bromide	0.548	7.56
Chlorine	<0.10	<0.10
Cyanide	<0.02	0.77
Ammonia Nitrogen	10.1	5020
Phosphate	4.0	11.5
Grease & Oil	885	107
Phenols	0.60	1.10
Cadmium	0.005	0.055
Chromium	<0.05	0.08
Copper	1.08	1.49
Lead	<0.05	0.40
Nickel	0.04	2.10
Silver	<0.01	0.20
Zinc	0.85	3.40
MEK	<1.0	2.24
MIBK	<1.0	1.74
Toluene	15.9	0.30
Xylene	1.60	0.43
Cyclohexanone	2810	107

Table 1.4.1 Recirculated Sample Characteristics (Source: MDS Laboratory Reports)

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Literature Review

2.1 Aerobic Treatability

Numerous individuals have investigated and reported on principles of biological activity including the metabolic processes involved in aerobic decomposition. This section reviews literature dealing specifically with the aerobic treatability or decomposition of wastewater pollutants.

Wastewater pollutants can be either organic or inorganic compounds. Inorganic pollutants generally cannot be destroyed so their treatment is generally via a more physical form in which the inorganic is converted to a sludge. Organic pollutants on the other hand, can be destroyed. The most common method for treating organic pollutants is to degrade them by biological oxidation (Klute and Hahn, 1990, p. 449). Aerobic treatment is a type of biological oxidation treatment used widely for treating or stabilizing domestic and industrial wastewaters. Aerobic processes include trickling filters, activated sludge units, rotating biological contactors (RBC), and stabilization ponds. The common factor in each of these very different processes is the use of air (oxygen) for the metabolism or biodegradation of organic matter.

Biodegradation is the destruction of a chemical compound by the action of microorganisms. Degradation can be of three degrees: complete mineralization of the compound by microbes to carbon dioxide and water, oxidation (metabolized) by microbial action to the extent that the compound has lost its characteristic properties, and nondegradable or molecularly recalcitrant. A material is classed as readily degradable when all the necessary specific enzymes needed for its decomposition pathway are present in the biomass (activated sludge or trickling filter film) and all reactions are allowed to proceed for the breaking down of the material. If one or more of these specific enzymes is

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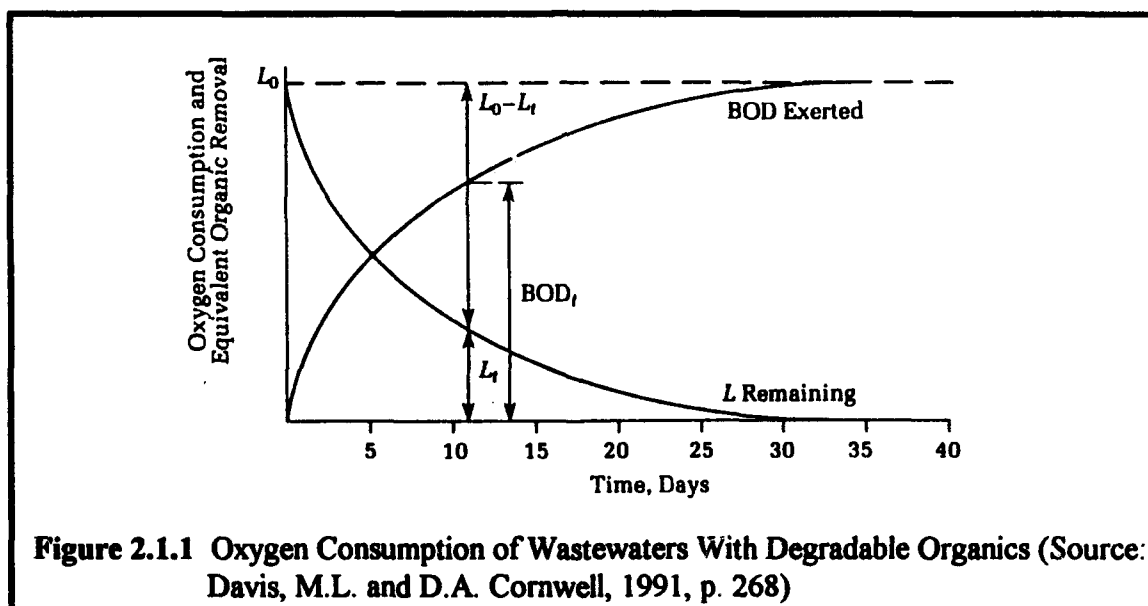
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missing or present in insufficient amounts, the material will be degraded only slowly or not at all. These materials are referred to as non-biodegradable, poorly biodegradable or incompletely degradable. In principle, all compounds synthesized by microorganisms should be capable of decomposition by microorganisms, some rapidly, others slowly. Problems are encountered when man-made synthetic compounds are entered into the picture. The degradability of these compounds is determined by its structure and reaction conditions like loading, residence time, and concentration (Mudrack and Kunst, 1986, p. 40-41). Microorganisms are capable of utilizing a wide range of chemical compounds, both inorganic and organic. Aerobic wastewater treatment relies on a mixed biological culture consisting of a variety of microorganisms. The treatment unit (i.e., activated sludge tank) is considered to be the reaction vessel holding the biological culture in a controlled environment to promote growth of microorganisms through the extraction of colloidal and dissolved compounds in the influent wastewater. In aerobic microorganisms, the tricarboxylic acid (TCA) cycle is the main mechanism for generating necessary enzymes. The further oxidation of these enzymes is linked to an electron transport chain which produces biological energy. Oxygen is a key element in this process as it is the terminal electron acceptor and in many cases is incorporated into molecules of the substrate acting as a catalyst for other reactions. The problem for aerobic microorganisms supplied wastewater with chemical compounds is the difficulties encountered by the microorganisms in converting the compounds into an intermediate that can be used in the TCA cycle. A. G. Calley et al. (1976) provides detailed discussion on how compounds can affect the rate of degradation of each other antagonistically or synergistically.

Davis and Cornwell (1991) explained the process of aerobic decomposition by relating the amount of oxygen consumed to the amount of organic matter that is degraded.

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Their premise was that the introduction of oxygen-demanding material, either organic or inorganic, into a water source causes the depletion of the dissolved oxygen in the water. To predict the extent of oxygen depletion, it is necessary to know how much waste is being discharged and how much oxygen will be required to degrade the waste. Figure 2.1.1 depicts the results obtained by measuring the daily oxygen consumption of a wastewater sample containing degradable organic matter. The rate of oxygen depletion is rapid during the first few days as the concentration of organic matter is high, but as the concentration of organic matter decreases, so does the rate of oxygen consumption.



Viessman and Hammer (1993) utilized the following general overall reaction to describe how reduced soluble organic compounds are oxidized to end products of carbon dioxide and water in the aerobic degradation process.



The energy stored in organic matter is released in the process by dehydrogenation of substrate followed by transfer of hydrogen, or electrons, to an ultimate acceptor. Aerobic

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metabolism using oxygen as the ultimate hydrogen acceptor yields the greatest amount of energy. The chief use of this energy is for the synthesis of new cellular material. The maximum rate of synthesis occurs simultaneously with the maximum rate of energy yield. In heterotrophic metabolism of wastewater organics, the maximum rate of removal of organic matter occurs during maximum biological growth. In aerobic metabolism, biologically available carbon is generally the limiting factor as an abundance of oxygen creates no shortage of hydrogen acceptors. In comparison to other processes, aerobic processes result in complete metabolism and synthesis of the substrate, ending in large quantities of biological growth.

Viessman and Hammer (1993) further classified biodegradable organic matter in wastewater in three general categories: carbohydrates, proteins, and lipids. Carbohydrates provide microorganisms with carbon. Proteins provide microorganisms with amino acids. Lipids provide microorganisms with fatty acids. Nonbiodegradable organic matter in wastewater includes lignin, a polymeric noncarbohydrate material; cellulose; saturated hydrocarbons; and alkyl benzene sulfonate, a synthetic detergent. These compounds are biodegradable to an extent, but due to time limitations in water treatment processes they can be considered nondegradable. These compounds make up about 20% - 40% of the organic matter found in wastewater, (Viessman and Hammer, 1993, p. 533). Supporting this statement, Gaudy and Blachly (1985) determined that although biological treatment for removal of soluble waste organic substrates has proven highly successful, treatment efficiency is seldom, if ever, 100%. Of the residual organic material, more than 90% is subject to biological metabolism at long cell retention times. Hao and Li (1987) showed how the nondegradable or slowly degradable organics exhibit

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a significant effect on the kinetic constants, specifically the substrate removal rate, measured in an activated sludge unit.

2.2 Principles of Paint

Waterer (1968) stated that it is probable that more upholstery leather goes into automobiles than into domestic furniture. This statement is likely to still be valid today. The leather required for this purpose has a sprayed paint and/or surface coating that allows the leather to be supplied in any color and any shade. The terms paint and surface coatings are used interchangeably in the paint industry. Surface coating is a more general description of any material that is applied as a thin continuous layer to a surface. Paint is more often used to describe pigmented materials. The purpose of paints and coatings is two-fold: to protect and to decorate. Lambourne (1987) and Letsky (1960) provide detailed reviews of the history of paints and surface coatings from its prehistory uses by stoneage man; during the middle ages where Europeans recognized the protective value of coatings for paintings, furniture and ship building; and through the industrial revolution where scientific discovery allowed the use of artificial pigments, solvents, resins, plasticizers, and films for the decorative finishing and protection of surfaces. Today, the coatings industry is a \$30 billion dollar worldwide market (EPA & ICF Consulting, 1990, p. 44).

Letsky (1960) also reviews the finishing of leather. Early finishes to leather used materials like blood, albumin, and alkaline solutions of shellac. These finishes gave a tough protective finish. Cellulose lacquers, nondrying oils and semi-drying alkyds were also used for leather finishing. Current leather finishing practices require thinner, flexible films that are lower in pigment. This is achieved through the use of modern painting

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procedures that include composite systems in which several thin films, some containing pigments, are applied to the surface.

Turner (1988) introduces the basic principles of paint chemistry. There is a multitude of different paints or surface coatings, but they all are formulated on the same basic principles and contain three main ingredients: pigments, film-former or binder, and liquid or diluent. The term solvent is a term loosely used denoting any liquid or diluent used in paint. Many different liquids or solvents are used in paints to carry the pigment and the binder including: water, paraffins, terpenes, alcohols, esters and ketones. Water-based paints have been and will continue to be of major use as legislation, economics, and world petroleum shortages encourage the use of decreasing amounts of volatile organic solvents. Randall (1992) states that the main driving forces behind the changes in paints and coatings toward water-based mixtures has been the environmental regulations and health concerns of the solvents used. Restrictions on volatile organic compounds and the reformulation process has been going on for many years. Organic solvents, however, do find continued use in specialized areas as water is not always an ideal paint liquid. Water has a limited miscibility with many of the film-formers or resins used in some paints. Some of the factors affecting the choice of solvents and solvent mixtures include solvency, viscosity, boiling point and evaporation rate, flashpoint, chemical nature, toxicity and smell. Table 2.2.1 shows some common solvents used in leather finishing and their properties. Burrell (1955) suggested that two factors governed the solvency of a liquid: the hydrogen bonding capacity of the liquid and the solubility parameter. The hydrogen bonding capacity can be either weakly bonded (Group I), moderately bonded (Group II), or strongly bonded (Group III). The solubility parameter is a measure of the attractive force between the liquid molecules. Film-formers or resins have a solubility parameter

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range for each of the three groups of solvents. Table 2.2.2 lists some common film-formers and their corresponding solubility parameter ranges. In many cases, a resin will not dissolve in a single solvent, but will dissolve in a mixture of that solvent and another solvent as the mixture's solubility parameter becomes the average of the parameters.

Solvent	Formula	Solvency H-Bond	Solubility	Viscosity	Boiling Point (°C)	Flash Point (°C)
Water	H ₂ O	III	23.4	1.002@20°C	100	None
Ketones						
MEK	CH ₃ COC ₂ H ₅	II	9.3	0.423@15°C	80	-4
MIBK	CH ₃ COC ₂ H ₂ (CH ₃) ₂	II	8.4	0.546@25°C	116	16
Aromatic Hydrocarbons						
Toluene	C ₆ H ₅ CH ₃	I	8.9	0.550@25°C	111	4
Xylene	C ₆ H ₄ (CH ₃) ₂	I	8.8	0.586@20°C	140	27
Aliphatic Hydrocarbons						
Cyclohexanone	CH ₂ CH ₂ H ₂ C CH ₂ CH ₂ CH ₂	I	8.2	0.890@25°C	81	3

Table 2.2.1 Solvent Properties (Source: Turner, G.P.A., 1988, p. 112-115)

Resin	Commercial Name	Chemical Type	Group		
			I	II	III
N/C, RS25cps		Nitrocellulose	11.1-12.7	7.8-14.7	14.5
Epikote 1001		Epoxy Resin	10.6-11.1	8.9-13.3	0
45% O.L linseed glycerol phthalate		Alkyd	7.0-11.9	7.4-11.0	9.5-11.9
CAB 1/2 sec		Cellulose Acetate Butyrate	11.1-12.7	8.5-14.7	12.7-14.5
Acryloid B-72		Acrylic Copolymer	10.6-12.7	8.9-13.3	0

Table 2.2.2 Solvent/Resin Properties (Source: Turner, G.P.A., 1988, p. 119)

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Viscosity is the liquid's internal resistance to flow. There are three essential facts about viscosity: as the solids content of the solution rises, so does the viscosity; high molecular weight resins give more viscous solutions; and the viscosities of the solutions will be proportional to the viscosities of the original solvents (Turner, 1988, p. 120-122). The boiling point (BP) and evaporation rate control the flow of paint. In this respect, solvents are graded into three groups: low boilers (BP<100°C) are used in spray paints as the solvent will evaporate between the application nozzle and the surface being painted; high boilers (BP>150°C) are used in applications where the paint must be kept fluid for longer periods as in brushed paints; and medium boilers (BP 100°C - 150°C) are used where ease of flow is necessary at first followed by quick set-up. The flashpoint is important as it is a measure of the flammability or fire risk. Care must be taken in the formulation of paints to abide by governing regulations and ensure precautions are taken in the application process to avoid risks of ignition. The chemical nature of solvent compounds demands precautions as solvents are chemicals which can react with other paint ingredients. Other precautions in formulating paints include toxicity and smell. Some solvents are poisonous or harmful. Threshold limit values (TLVs) have been established for concentrations of many substances in the work environment including solvents used in paint processes (Turner, 1988, p. 123-125).

2.3 Governing Regulations

Wastewater discharge requirements in the United States have evolved significantly since the establishment of the Federal Water Pollution Control Act of 1972 and the Clean Water Act of 1977. This section reviews some of the recent changes in regulations that may impact upon the decisions made from the results of this project.

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Gemar (1991) reported that as of July 24, 1990, new regulations under the National Pretreatment Program restricted industries from discharging process wastewater containing hazardous wastes to POTWs. The regulation placed limits on the types of waste that can be discharged by an industrial facility to a POTW, requires POTWs to institute pretreatment control programs, and requires industries discharging more than 15 kilograms of nonacute hazardous waste and any amount of acute hazardous waste per month to a POTW to notify the POTW, the state hazardous waste permitting authorities, and the regional EPA hazardous waste division. The regulation prohibits the discharge of oil and grease, ignitables, toxic gases, or hauled wastes. Koorse (1993) reported that industries traditionally were only subject to three types of pretreatment requirements: general prohibitions, specific prohibitions, and categorical standards. Few industries were subject to toxics limits imposed by their POTWs, because few POTWs received toxics limits in their National Pollution Discharge Elimination System (NPDES) permits. With the new toxics regulation POTWs are imposing strict pretreatment standard on upstream industrial dischargers. Prothro (1993) reported that the National Sewage Sludge Rule signed November 25, 1992 further requires communities to develop and implement effective pretreatment programs to ensure that industry removes toxic and other harmful pollutants from its wastewater before it flows to POTWs where those pollutants could end up in biosolids or in waterways. This new rule addresses three general categories of beneficial use and disposal practices: land application of biosolids, surface disposal at dedicated sites or in wastewater solids-only landfills, and incineration of biosolids. Prescott (1992) discussed how serious the EPA was about enforcing the new pretreatment rules. The EPA has taken action against 130 POTWs in over 32 states that failed to administer or enforce a local pretreatment program.

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EPA & ICF Consulting (1990) discussed how the Land Disposal Restriction Rule (Section 268.3) prohibits the dilution of restricted wastes as a substitute for adequate treatment to meet the treatment standards. The provision ensures that no individual circumvents the intent of EPA's concentration-based regulations by simply adding material to wastes that do not meet the treatment standards, rather than treating the wastes. Dilution, as a necessary part of the waste treatment process, is allowed under the final rule. Section 268.41 of the Land Disposal Restriction Rule discusses the treatment standards necessary for solvents. Methyl ethyl ketone, xylene, toluene, methyl isobutyl ketone, and cyclohexanone are considered spent solvents under the land disposal restrictions rule when they are used to solubilize or mobilize other constituents. A solvent is considered spent when it has been used and is no longer fit for use without being regenerated, reclaimed, or reprocessed. Table 2.3.1 lists the treatment standards for solvents in wastewaters. Wastewater in this table is defined as solvent-water mixtures containing less than or equal to 1 percent total organic carbon (TOC) by weight. All other spent solvent wastes include wastewaters containing greater than 1 percent TOC, solvent containing solids, sludges and contaminated soils. These treatment standards were established based on best available technology performance.

Spent Solvent Waste	Wastewater Concentration Standard (mg/L)	Other (mg/L)
Xylene	0.05	0.15
Toluene	1.12	0.33
Methyl Ethyl Ketone (MEK)	0.05	0.75
Methyl Isobutyl Ketone (MIBK)	0.05	0.33
Cyclohexanone	0.125	0.75

Table 2.3.1 Solvent Treatment Standards (Source: EPA & ICF Consulting, 1990, p. 9)

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As of November 8, 1988, solvent-water mixtures, solvent-containing sludges or solids, and solvent-contaminated soil containing less than one percent total solvent constituents; as well as wastes generated by small quantity generators of 100 to 1,000 kg/month of hazardous wastes were prohibited from disposal (EPA & ICF Consulting, 1990, p. 9). Section 313 of Title III of the Superfund Amendments and Reauthorization Act (SARA) among other requirements requires industries within the standard industrial classification codes 20-39 (leather finishing SIC 3199) to report to EPA and their state any releases of chemicals to air, water, or land and those transferred to off-site facilities in excess of the threshold quantities.

2.4 Applicable Studies

Numerous studies have been reported on the biodegradation of various organic compounds and their effects on the activated sludge performance of publicly owned treatment works (POTW).

Lewandowski (1990) determined that bench-scale reactor testing could be used to estimate the amount of throughput and magnitudes of degradation rates to indicate a POTW's potential for handling industrial wastes. He further showed that organic compounds could be biologically treated by mixed liquor from any POTW, not exclusively by a POTW that had experienced significant prior exposure. Microbial adaption to the organic waste was found to be quite rapid.

The term inhibitor is often used to denote a toxicant at concentrations below that which stops all microbial activity, causes a reduction in the rate at which a biomass functions. Volskay, Grady and Tabak (1990) studied 33 RCRA-listed compounds to determine their impacts on activated sludge operations. Their study utilized respirometric testing to quantify inhibitory concentrations of the various compounds. Of the volatile

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organic solvents used in the leather finishing industry (MEK, MIBK, toluene, xylene, and cyclohexanone) all were found to have a less than 50% inhibition effect on activated sludge at a test concentration of 1000 mg/L. The highest factor was for toluene (48%). From this study, the conclusion is drawn that there should be little to no effect on the kinetic parameters of the activated sludge system due to the addition of leather finishing volatile organic compounds at concentrations below 1000 mg/L.

In the leather finishing process, a large amount of ammonia is used when formulating water-based surface coatings to neutralize the high acid values obtained when carboxyl groups are incorporated into the polymers. Ammonia is an atmospheric pollutant that can be absorbed by waterways leading to eutrophication nuisances. Ammonia also reduces the disinfecting power of chlorine causing increased water treatment costs. Abeliovich and Azov (1976) determined that ammonia can also be a toxicant to plant life in waterways subjected to sewage loads. Ammonia in waste treatment is produced during the decomposition of organic material within wastewater. Nitrate is the end product of microbial breakdown of organic nitrogen in aerated wastewater. Nitrate results when nitrifying bacteria are present to oxidize the ammonium ions released by microbial attack on the nitrogen containing substrate. Problems associated with high nitrate concentrations include methaemoglobinaemia, eutrophication and in vivo synthesis of nitrosamines which are known to be carcinogenic. Nitrite is an intermediate in autotrophic nitrification and in the reduction of nitrate to ammonium. It is important to minimize or remove the nitrogenous constituents in wastewater to both minimize the toxicity of the water and to reduce its total oxygen demand. Nitrification can be controlled by maintaining a significant population of nitrifying bacteria in an activated sludge tank. A reliable system is one which utilizes a separate tank which follows the one used for removing organic

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materials. This tank can be operated at a longer solids retention time to maintain a population of nitrifying bacteria (Dart and Stretton, 1980, p. 9-13 and 136).

Cheremisinoff (1986) reported that United States industries spent \$5-billion to treat hazardous wastes. That amount was expected to double by 1990, when industries were expected to be treating over 280 million metric tons per year of waste. Treatment methods recommended by EPA & ICF Consulting (1990) for non-halogenated solvents like cyclohexanone, toluene, MEK, and MIBK include solvent reclamation, devolatilization, physical blending, fuel supplement, or incineration. Wastewater treatment was not recommended for highly concentrated waste streams, but it was noted that the potential for this method of treatment has not been fully utilized and needs extensive testing to define acceptable conditions for various substances (EPA & ICF Consulting, 1990, p. 54 and 103). Biological wastewater treatment can result in the generation of solid residuals that would be classified as hazardous. Also, the EPA is currently studying the possible regulating of air emissions from POTWs treating certain compounds (EPA & ICF Consulting, 1990, p. 107). Aqueous wastes containing solvents are often treated onsite to reduce their toxicity and chemical or physical properties. For large volumes of wastewater with very low solvent concentrations, the most common treatment systems either involve biological degradation or stripping with air or steam. Stripping is often followed by treatment or recovery to control air emissions. Recycling by steam stripping is favored because it produces a more concentrated solvent waste stream than air stripping. Activated sludge treatment may be used to treat dilute solvent-bearing wastes that contain less than one percent suspended solids. The process is frequently used for solvent-laden wastes from organic chemical manufacturing, petroleum refining, paint and ink formulation and gum and wood chemicals. Disadvantages include the disposal of large

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quantities of sludge and potential need for air emission control (EPA & ICF Consulting, 1990, p. 125).

Solvents used in painting applications are generally blended products and formulated to meet specific volatility and solubility requirements, their reclamation for reuse as paint diluents is not generally recommended, but reclamation for reuse in cleaning applications is recommended (EPA & ICF Consulting, 1990, p.80). Landau (1990) investigated the potential applicability of supercritical fluid extraction for detoxifying hazardous and toxic components from paint production wastes of small quantity generators. The process was found to offer the possibility for recovering solvents and solids from paint wastes. Removals greater than 50 percent were reported and supercritical fluid extraction was found to be more effective at removing paint than conventional distillation.

Govind and Dobbs (1991) utilized an integrated fate model to predict the fate of organics in a wastewater treatment plant. They validated the model using experimental data from a pilot-scale facility. The degradability of MEK was predicted in their model to total 58.6% while their experimental data indicated 94.3% biodegradation of MEK. The degradability of MIBK was not predicted in their model, but their experimental data indicated 95% biodegradability. The degradability of toluene was predicted in their model to total 89.4% while their experimental data indicated 72% biodegradation. The degradability of xylene was predicted in their model to total 42.7% while their experimental data indicated 66% biodegradation. The degradability of cyclohexanone was predicted in their model to total 83.6% while their experimental data indicated 81.1% biodegradability. Grady (1990) investigated the status and potential for biodegradation of toxic organic chemicals. His exhaustive review of a multitude of literature showed that

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treatment systems for synthetic organic chemicals need not be exotic. In fact, conventional biological treatment systems as those at POTWs are effective in removing such chemicals. Biodegradation of such chemicals was determined to occur best when they are fed in dilute form to diverse microbiota in the presence of adequate nutrients and secondary substrates, all of which are met by POTWs. Grady further states however, that activated sludge was also unable to meet the new effluent guidelines for 33 chemicals on the RCRA list of standards for hazardous organic chemicals even when powdered activated carbon was added to the system. Grady suggests that a mixture of environments (aerobic, anaerobic, anoxic) may provide more successful destruction of some compounds. He points out that toluene and xylene have been shown to be degradable in anoxic as well as aerobic environments. Kim, Anderson and Zemla (1992) found that a mixture of environments successfully degraded organic compounds with the added benefit of decreased amount of solids production, degradation of nitrogen, a lower oxygen requirement, and potential energy recovery from organics in wastewater.

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Materials and Methods

3.1 Aerobic Seed Culture Reactor

A master culture reactor (MCR) was used to provide an acclimated seed culture having identifiable and repeatable characteristics so that measurements made at different times and with different sets of tests would have a common microbial and biochemical basis (Kim, 1991). The MCR consisted of a 10-liter plexi-glass vessel containing 8 liters of mixed culture obtained from an activated sludge aeration tank. Filtered air was pumped into the reactor through an air stone providing continuous and thorough aeration of the culture. No mechanical mixing was necessary. The MCR was operated under the following conditions:

1. A feedstock of 905 g/L COD derived from a mixture of solvent-based coating, water-based paint and cleanup wastewaters diluted in Nutrient/Mineral/Buffer (NMB) medium,
2. A temperature of 20°C,
3. Hydraulic and solids retention time (SRT) of 10 days,
4. A draw and fill feed schedule,
5. A COD loading rate of 1.0 g/L-d.

3.2 Nutrient Mineral Buffer Medium

The formulation of stock solutions for the NMB used in this project is given in Appendix A.

3.3 Materials

The culture biomass was obtained from the activated sludge aeration tanks at the University Park Wastewater Treatment Plant, State College, Pennsylvania. All other

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chemicals were purchased from Fisher Scientific, Pittsburgh, PA or Hach Chemical Company, Loveland, CO.

3.4 Testing Program

The study was accomplished in two phases. Phase I was conducted during the Spring Semester 1993 and consisted of initial aerobic respirometer tests and mass balance analysis of the Seton Company wastewaters. The results of Phase I were published in a report to the Seton Company, Environmental Resources Research Institute (ERRI) project number 92C.II40R-1. Phase II was conducted during the Summer Semester 1993 and consisted of bench-scale reactor tests with additional aerobic respirometer and gas chromatographic analysis of the effluents generated by the bench-scale reactors. As discussed, the treatability test program consisted of three test procedures: aerobic respirometer tests, mass balance load analysis and bench-scale reactor tests. Aerobic respirometer tests offer a means of measuring oxygen uptake of wastewaters or specific organic chemicals continuously over a period of time. This oxygen uptake is useful in assessing the effect of known amounts of toxic compounds on the oxygen uptake reaction of a wastewater or organic chemical, determining inhibitory concentrations of a pollutant, estimating oxygen requirements for complete oxidization of compounds, and estimating the degree of biodegradation of specific organic compounds (Young, 1992). These batch tests provided an indication of the response of the test culture to a single batch dose of a test waste. Some possible variations in response patterns are illustrated in Figure 3.4.1 and are described as follows:

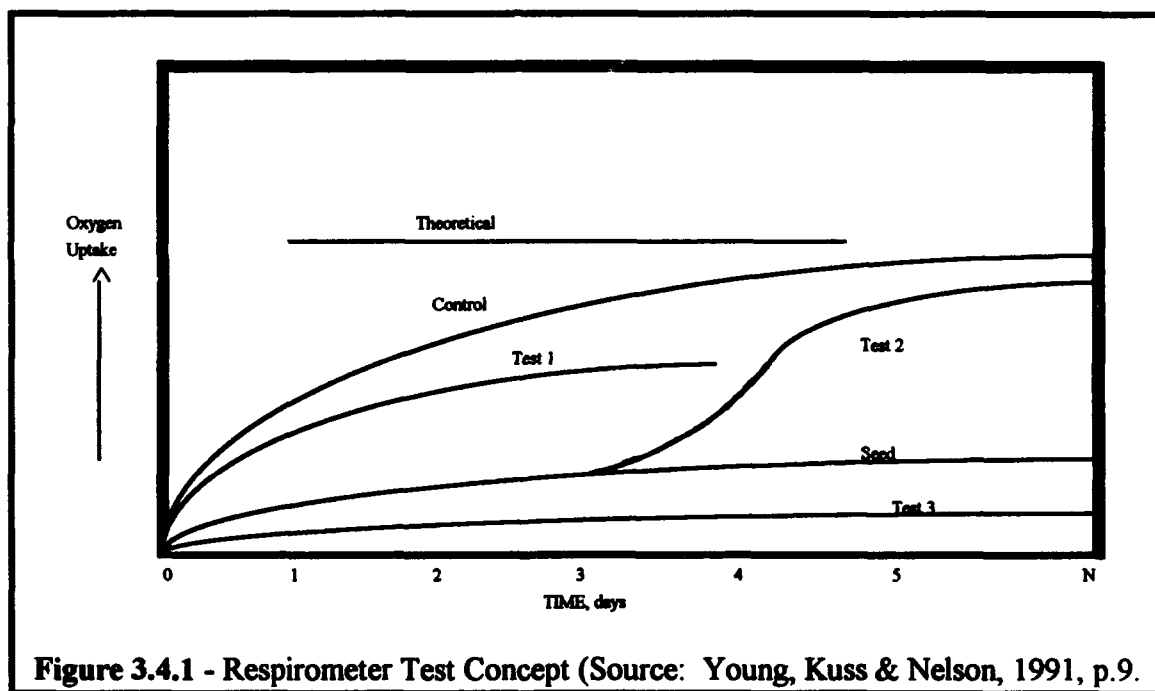
CONTROL: Represents the base for comparison. If the test waste is toxic or has potential treatability problems, the oxygen uptake curves will lie below the oxygen uptake curve for the control.

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Test 1: Indicates that the organic material in the test waste degrades at essentially the same rate as the control, but that not all the organic material may be degradable.

Test 2: Indicates that the organic materials in the test waste degrade to essentially the same extent as those in the control but that a period of acclimation or adjustment is needed.

Test 3: Indicates that the test waste is toxic to the seed culture.



The mass balance analysis of loadings required the characterization of the various waste effluents. Mathematical analysis of this data determined the amounts of suspended solids, biochemical oxygen demand, total chemical oxygen demand, soluble chemical oxygen demand, ammonia nitrogen, and sludge generation that could be expected at the POTW if the Seton Company was allowed to discharge their waste effluents (illustrated calculations are provided in Appendix B).

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Bench-scale reactor tests were conducted to determine the response of aerobic cultures to longer-term feeding of sample wastewater. This is not possible in batch-fed respirometer tests. This approach involved feeding a wastewater sample semi-continuously to an active culture over a period of 30 days. These bench-scale reactors operated much the same way as the MCR. Nine reactors were fabricated out of six-inch diameter plexi-glass. Each reactor was designed for a capacity of 10 liters with sufficient free board to prevent splashing or contamination of the other reactors. Polyvinylchloride (PVC) pipe end caps were attached to the bottoms of each reactor providing a conical bottom ensuring that no sludge would be entrapped in the bottom or sides. Taps were bored into the end caps to allow for drainage or removal of samples for testing. Air was pumped into each reactor via tubing that entered the tops of each reactor. An airstone was weighted to the bottom of each reactor to provide fine and diffused bubbles of air. The source air was filtered through a Balston Microfibre disposable filter unit and then bubbled through a four liter bottle containing three liters of distilled water. This apparatus was intended to rehydrate the dry source air in an effort to cut down on evaporation in the reactors. A gage pressure of 20 psi for the source air was found to provide sufficient aeration to keep solids suspended and well mixed in all the reactors.

Figure 3.4.2 shows the reactor apparatus used in this project. Columns 1, 2 and 3 were used for water-based paint wastes (booth 1, 2, 4 and cleanup water). Columns 4, 5 and 6 were used for solvent-based coatings wastes (booth 3 only). Columns 7, 8 and 9 were used for controls (ethanol solution only). The first reactor in each series represented an activated sludge unit operating at a 10 day SRT. These reactors received the raw waste feed. The second reactors in series represented another activated sludge unit operating at a 20 day SRT. The purpose of these reactors was to assess the effects of

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operating two activated sludge treatment units in series. These reactors received the clear water effluent from the first reactors as their only source of feed. The third reactor in each series represented an aerobic sludge digester. These reactors received the settled solids generated and removed from both the first and second reactors in each series as their only source of feed.

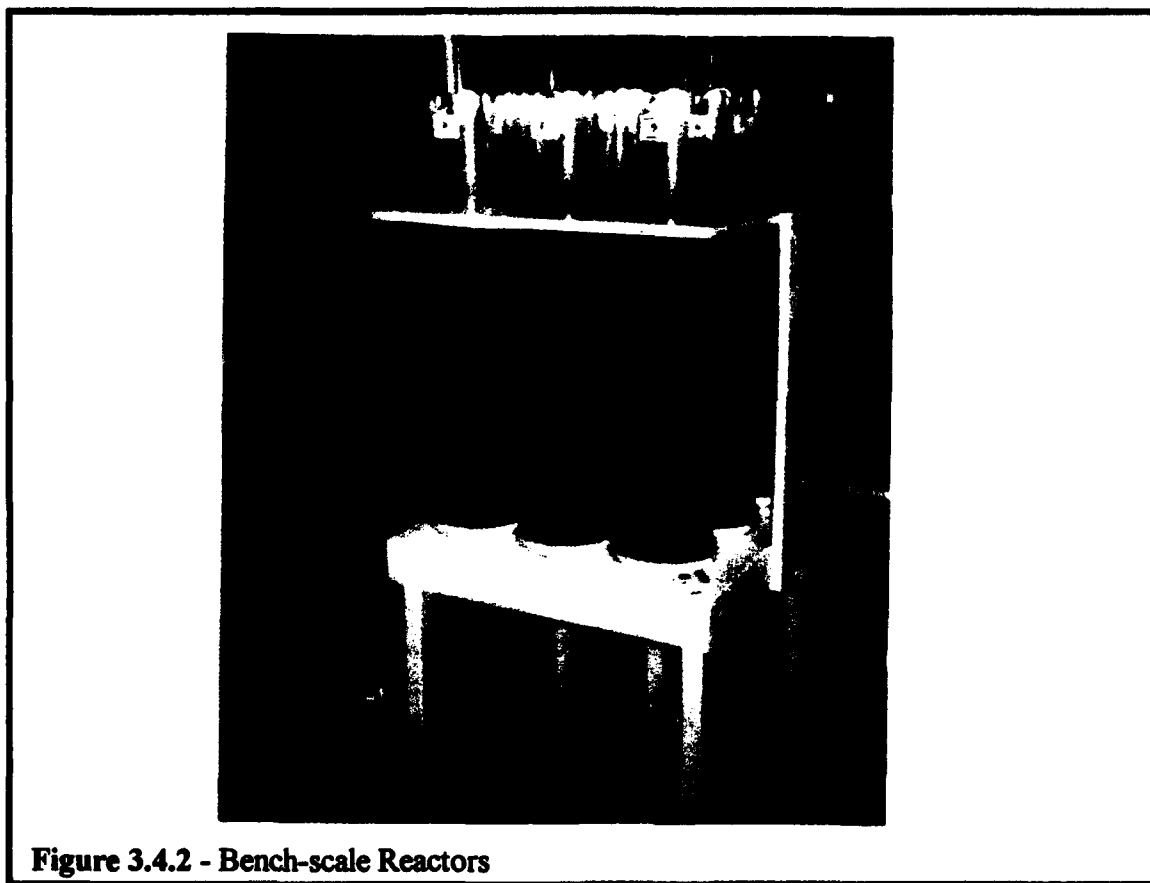


Figure 3.4.2 - Bench-scale Reactors

Daily operation of the bench-scale reactors consisted of a five-step procedure as outlined by the following:

Step 1 - Measure and record pH of all reactors. Turn off air to columns 3, 6 and 9 allowing the mixed liquor to settle for 10 minutes and recording the amount of settled

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solids. Decant 300 ml of clear water from the top of column 3, 6 and 9. Re-establish air to columns 3,6 and 9.

Step 2 - Drain 500 ml from the bottom of columns 2, 5 and 8 while air was running to ensure complete mixing. Using cone settler, separate solids from liquid saving solids for later use (see Step 4).

Step 3 - Drain 1000 ml from bottom of columns 1, 4 and 7. Using cone settler, separate solids from liquid saving solids for later use (see Step 4). Measure 500 ml of clear water from each of the samples (1, 4 and 7) and add to the respective second column, ie., 500 ml of clear water from column 1 added to column 2, 4 to 5, and 7 to 8.

Step 4 - Combine solids taken from columns 1, 4, and 7 to the solids taken from columns 2, 5, and 8 respectively. Measure 300 ml of each combined sample and add to columns 3, 6, and 9 respectively. If not enough solids were available to make 300 ml the shortfall was made up with tap water.

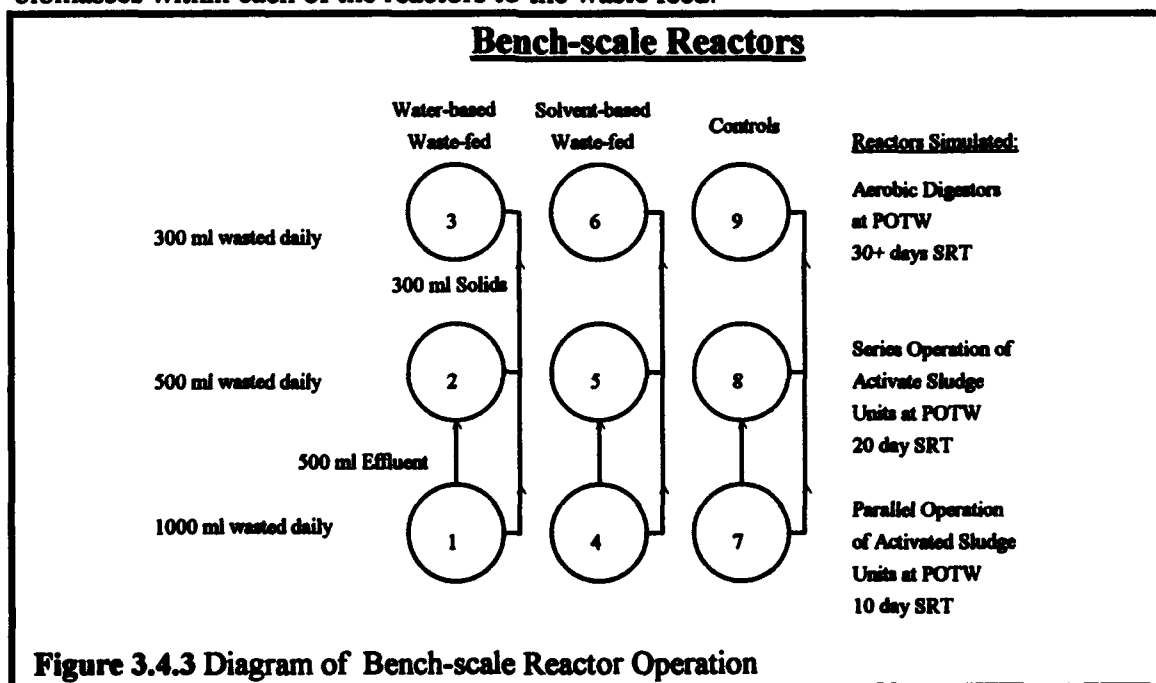
Step 5 - Appropriate amounts of feed solution were diluted to 1000 ml with NMB solution and added to columns 1, 4, and 7 respectively.

Figure 3.4.3 depicts a diagram that summarizes the operations of the bench-scale reactors used in the study.

The bench-scale reactors were filled with 10 liters of mixed liquor from the activated sludge process units at the University Park Wastewater Treatment Plant. An additional 100 ml of acclimated seed from the MCR was added to each reactor and aerated one day before the start of the test. The seed from the MCR was assumed to be well acclimated as it had been receiving continuous feeding of Seton wastewater for over six months. The bench-scale reactor test was initially started using only the Seton Company waste diluted with NMB as a feedstock. Ten days into the test the biomass of

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reactors 1 and 4 had been washed out of the reactors. It was determined that the Seton Company waste, fed in the same proportion as would be expected at the POTW, was insufficient in COD loading to sustain an adequate biomass concentration. The test was restarted using sufficient ethanol feedstock mixed with the Seton Company waste to maintain a 1 g COD/L/day loading rate in the first series of reactors. Appendix C contains calculations used to determine respective feed concentrations. Reactors 1, 2 and 3 (water-based paint residuals) were emptied into a large carboy, thoroughly mixed, and 10 liters were returned to each of the three reactors. The same mixing procedure was used on the solvent-based coatings fed reactors (4, 5 and 6) and then the control reactors (7, 8 and 9). The TSS content of the solvent and water-based waste fed reactors was roughly the same, but since sufficient COD loading was available in the control throughout the first test more biomass was generated and the resulting TSS were higher for the start of the second test. It is assumed that this restart of the test also allowed for a better acclimation of the biomasses within each of the reactors to the waste feed.



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Aside from daily measurements of pH and temperature, Table 3.4.1 shows the frequency and type of additional tests run during the bench-scale reactor test phase. The data obtained from these tests is summarized in tabular form in Appendix D.

3.5 Analytical Procedures

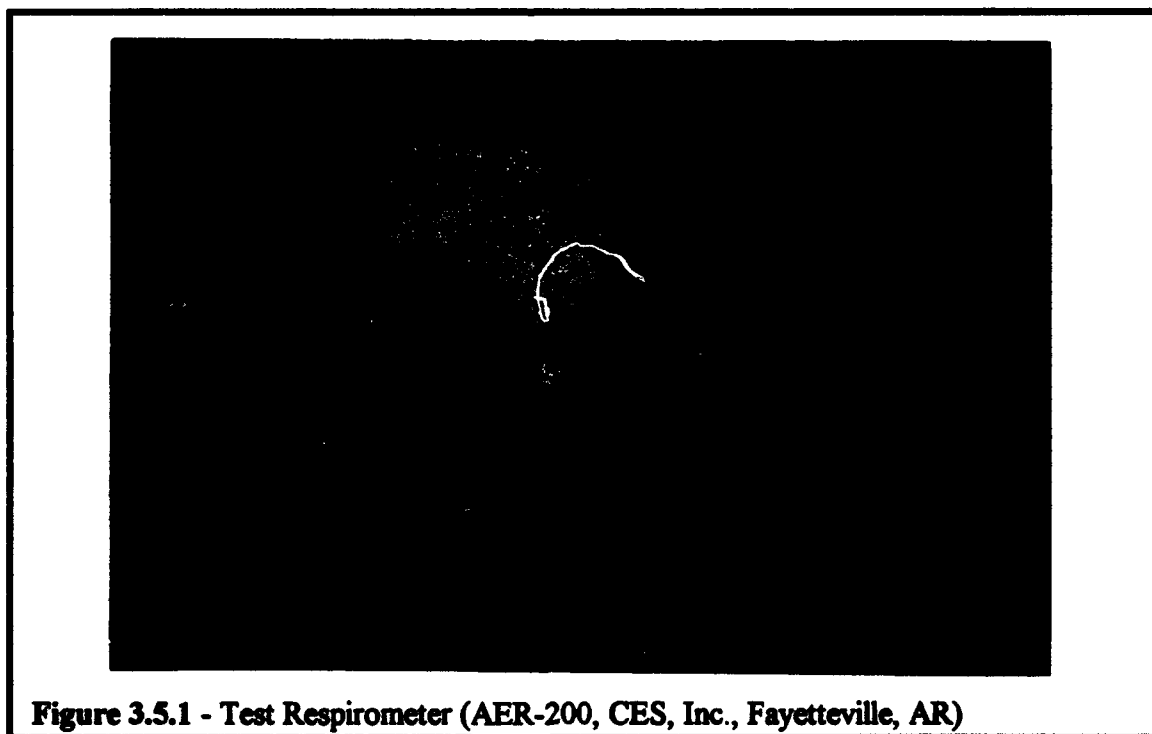
Oxygen uptake from the test reactors was measured by using an automatic aerobic respirometer (AER-200, Challenge Environmental Systems, Inc., Fayetteville, AR) which operates by counting bubbles as they pass between two detector elements in a plexi-glass flow measuring cell. Each bubble corresponds to 0.056 mg of oxygen. Figure 3.5.1 shows the system in operation. Tests were conducted according to respirometric methods (Young, 1992).

Day	Tests Conducted
1	TSS, VSS, SCOD, TCOD, Ammonia
3	TSS, VSS, SCOD, TCOD
5	TSS, VSS, SCOD, TCOD
7	TSS, VSS, SCOD, TCOD
9	TSS, VSS, SCOD, TCOD
11	TSS, VSS, SCOD, TCOD
13	TSS, VSS, SCOD, TCOD
15	TSS, VSS, SCOD, TCOD, Ammonia
20	TSS, VSS, SCOD, TCOD
25	TSS, VSS, SCOD, TCOD
30	TSS, VSS, SCOD, TCOD, Ammonia

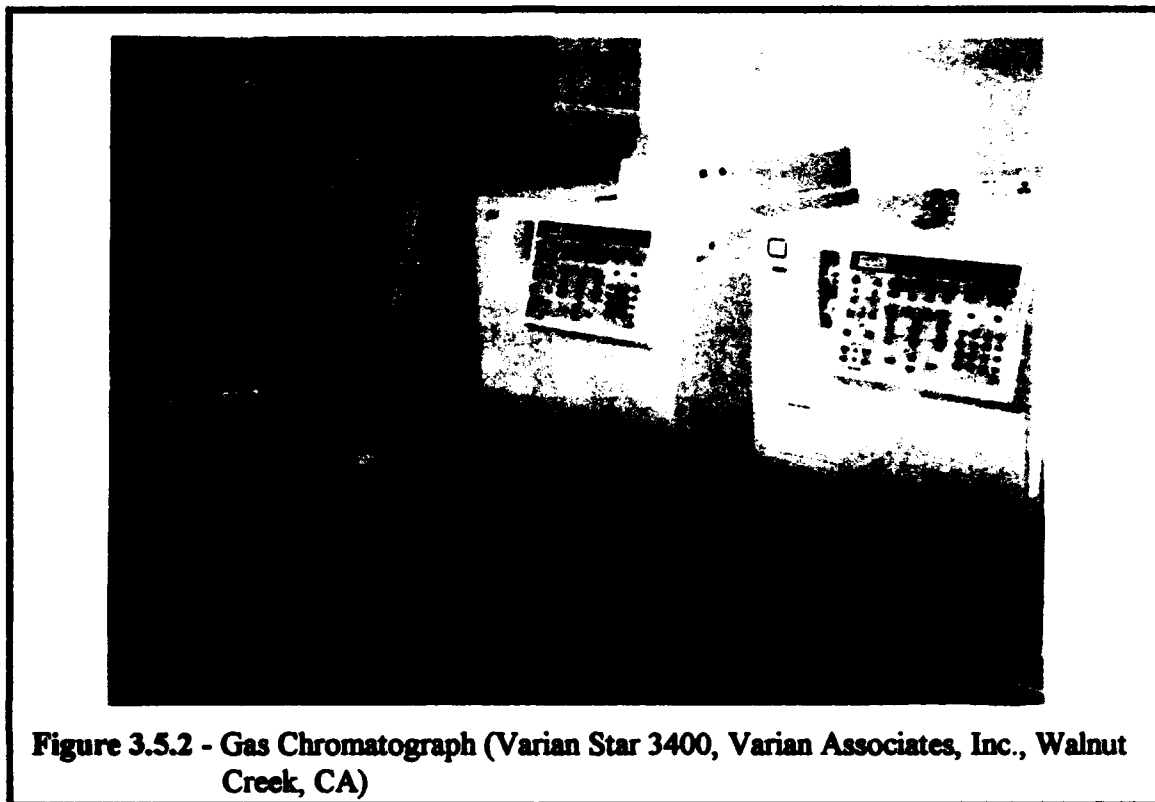
Table 3.4.1 Schedule of Sample Testing for Reactors

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The pH of the various wastes and cultures was measured using a Fisher Scientific Accumet 425 Digital pH/ion meter. Chemical Oxygen Demand (COD) was measured using Hach methods (Hach Chemical Company, Loveland, CO, 1985). Volatile suspended solids (VSS) and total suspended solids (TSS) were measured according to Standard Methods (American Public Health Assoc., Washington, D.C., 1992). Total Kjeldahl Nitrogen (TKN) was measured using a Hach Digestal apparatus and Hach methods for determination (Hach Chemical Company, Loveland, CO, 1985). Ammonia ($\text{NH}_3\text{-N}$) was measured using Hach methods (Hach Chemical Company, Loveland, CO, 1985). Gas chromatography (GC) analysis was conducted using a Varian Star 3400 system and Varian methods for analysis (Varian Associates, Inc., Walnut Creek, CA, 1991). Figure 3.5 2 shows the GC system in operation.



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Results

4.1 Discharge Analysis

Figure 4.1.1 shows the hydraulic effect of adding the Seton wastewater flows to the current POTW influent. Data used to build the graph of influent flow rates was obtained from the Saxton Borough Municipal Authority Wastewater Treatment Plant Discharge Monitoring Report - Supplemental Form S (NPDES, 1991-1992). Daily flow rates for October 1991 through October 1992 were plotted to yield the variably spiked, thin, solid line. The average of the daily flows was calculated (0.195 MGD) and plotted as the thick solid line. The maximum flow allowed under the Saxton POTW's NPDES is 0.4 MGD and is represented by the upper asterisk line.

The Seton Company's leather finishing process currently generates 4500 gallons of wastewater (4-1000 gallons spraybooth recirculation tanks plus 500 gallons of cleanup water). If the Seton Company was to be able to discharge this wastewater on one particular day the additional hydraulic load on the Saxton POTW will increase to an average daily load of 0.199 MGD as represented by the dot-dashed line on the graph. The Seton Company is considering expanding its operations with three more units generating a future hydraulic load of 8000 gallons (7-1000 gallon tanks plus 1000 gallons of cleanup water). Discharge of this wastewater on one particular day will increase the average daily load of the Saxton POTW to 0.204 MGD as represented by the dotted line on the graph. It can be seen from this graphical analysis that the hydraulic load from the Seton Company will have a limited impact on the Saxton POTW.

4.2 Mass Balance Analysis

Table 4.2.1 shows the results obtained through mass balance analysis of the various waste effluent samples. As is depicted, the data represents three possible

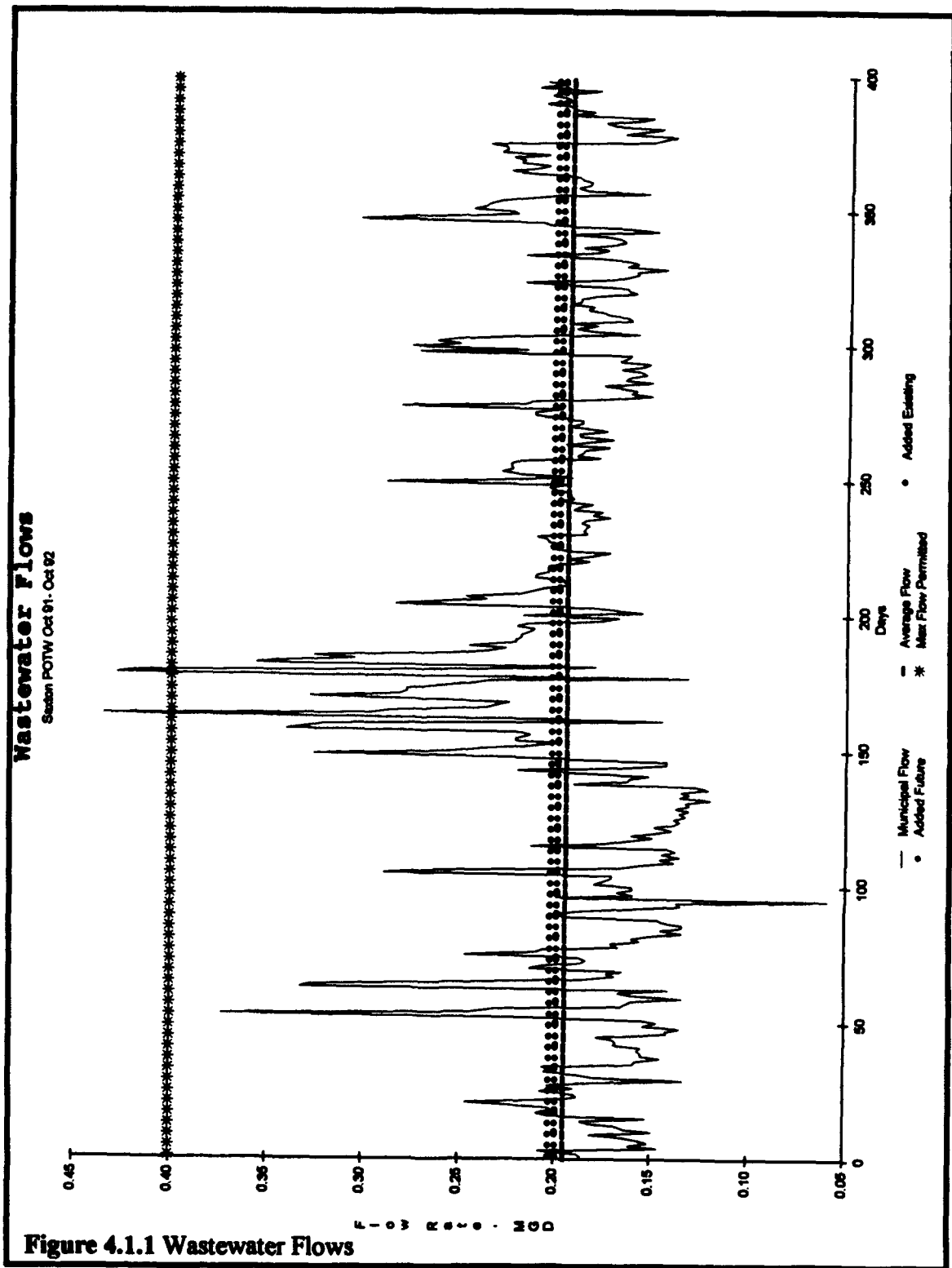


Figure 4.1.1 Wastewater Flows

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WORSE CASE - MONTHLY SITUATION					
OPTIONS	FLOW gpd@discharge	SS LOAD lb/day	BOD LOAD lb/day	NH3-N LOAD lb/day	SLUDGE lb/day
Water-Based Effluent					
Booths 1,2,4 & Wash Bay	3500	1176	953	22	974
Booths 1,2,4,5,6 & Wash Bay	6000	2017	1634	38	1670
Solvent-Based Effluent					
Booth 3 w/o removal	1000	65	182	33	112
Booth 3 w/removal	1000	3	29	2	14
Booths 3 & 7 w/o removal	2000	130	363	65	223
Booths 3 & 7 w/removal	2000	6	59	5	28
Totals					
Existing Ops w/o removal	4500	1241	1135	55	1086
Existing Ops w/removal	4500	1179	983	25	988
Future Ops w/o removal	8000	2147	1998	103	1893
Future Ops w/removal	8000	2023	1693	43	1697
Other					
Saxton POTW Existing Load	207000	226	326	52	254
Saxton POTW Design Load	400000	684	587	***	577
BEST CASE - DAILY SITUATION					
OPTIONS	FLOW gpd	SS LOAD lb/day	BOD LOAD lb/day	NH3-N LOAD lb/day	SLUDGE lb/day
Water-Based Effluent					
Booths 1,2,4 & Wash Bay	3500	33	26	0.62	27
Booths 1,2,4,5,6 & Wash Bay	6000	56	45	1	46
Solvent-Based Effluent					
Booth 3 w/o removal	1000	2	5	1	3
Booths 3 & 7 w/o removal	2000	4	10	2	6
Booth 3 w/removal	1000	0.09	1	0.07	0.38
Booths 3 & 7 w/removal	2000	0.17	2	0.14	1
Totals					
Existing Ops w/o removal	4500	34	32	2	30
Future Ops w/o removal	8000	60	55	3	53
Existing Ops w/removal	4500	33	27	1	27
Future Ops w/removal	8000	56	47	1	47
Other					
Saxton POTW Existing Load	207000	226	326	52	254
Saxton POTW Design Load	400000	684	587	***	577
WEEKLY SITUATION					
OPTIONS	FLOW gpd@discharge	SS LOAD lb/day	BOD LOAD lb/day	NH3-N LOAD lb/day	SLUDGE lb/day
Water-Based Effluent					
Booths 1,2,4 & Wash Bay	3500	163	132	3	135
Booths 1,2,4,5,6 & Wash Bay	6000	280	227	5	232
Solvent-Based Effluent					
Booth 3 w/o removal	1000	9	25	5	16
Booth 3 w/removal	1000	0	4	0	2
Booths 3 & 7 w/o removal	2000	18	50	9	31
Booths 3 & 7 w/removal	2000	1	8	1	4
Totals					
Existing Ops w/o removal	4500	172	158	8	151
Existing Ops w/removal	4500	164	136	3	137
Future Ops w/o removal	8000	298	277	14	263
Future Ops w/removal	8000	281	235	6	236
Other					
Saxton POTW Existing Load	207000	226	326	52	254
Saxton POTW Design Load	400000	684	587	***	577

Table 4.2.1 Waste Load Mass Balance Analysis

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situations involving the batch discharge of the process wastes from the booths: either monthly, weekly, or daily discharge. Data used to construct the three situation tables depicted in Table 4.2.1 was derived from laboratory analysis of samples taken from the six different unit processes in the Seton Company's operation: booths 1 and 2 are water-based paint effluents, booth 3 is a solvent-based coatings effluent, recycle water is the alum treated water from booth 3, holding tank water is the composite water from booths 1 and 2 and cleanup water. Table 4.2.2 shows the resultant characteristics of each of the samples. It should be noted that the samples taken represent process waters that have been recirculated for 36 days of operation. No sample was taken of booth 4 wastewater as this booth was not in operation at the time of sampling.

SAMPLE	pH	TSS mg/L	VSS mg/L	SCOD mg/L	TCOD mg/L	TKN mg/L	NH ₃ -N mg/L
Recycle (Alum Treated)	6.45	370	160	9500	10300	735	298
Cleanup (Washbay)	8.64	8800	5400	21000	31500	420	158
Booth 3 (Solvent-based)	6.22	7800	3600	65000	65500	4830	3920
Booth 2 (Water-based)	7.56	31400	16900	49000	63100	4380	1440
Booth 1 (Water-based)	8.13	75500	48500	121000	194200	5957	4260
Holding Tank (Composite)	8.90	40300	32000	97500	151700	1650	760

Table 4.2.2 Characterization of Recirculated Waste Effluent Samples After 36 days of 7 day/week Operation

In constructing the three situation tables in Figure 4.2.1, the flows were determined using the fact that each spraybooth possesses a 1000 gallon recirculating wastewater tank. It was assumed that an average cleanup volume of water was 500 gallons. For the future expanded operations, the same rationale was used with the

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assumption that since operations would essentially double, so too would the amount of cleanup water used. The existing and design load flows for the treatment plant were taken from the 1992 Chapter 94 Municipal Wasteload Management Report and Basic Design Criteria obtained from the plant operator and municipal engineering consultant (Gwin, Dobson & Foreman, 1993). The suspended solids (SS) load was calculated using the TSS determined through laboratory analysis (multiplying the flow by the concentration of suspended solids and converting to pounds per day). The TSS for the holding tank sample was used to represent that expected from the mixed water-based wastewater. The TSS for the booth 3 sample was used to represent that expected from the solvent-based wastewater. The TSS for the recycle sample was used to represent that expected from the alum treated solvent-based wastewater. Those options listed in the left column of Figure 4.2.1 that designate "with removal" indicate calculations made using the recycle sample that was alum treated. Those options designating "without removal" indicate calculations made using the solvent-based sample characteristics. The existing and design SS loads for the treatment plant were taken from the 1992 Chapter 94 Municipal Wasteload Management Report (Gwin, Dobson & Foreman, 1993). To determine the BOD load on the treatment plant the BOD measurement used must correlate with the five-day BOD (BOD_5) used to determine the BOD design load capacity in the 1992 Chapter 94 Municipal Wasteload Management Report. The BOD_5 is assumed to be two-thirds of the ultimate biochemical oxygen demand (BOD_U). The BOD_U load was calculated using 50% of the COD determined through laboratory analysis (multiplying the flow by the concentration of BOD and converting to pounds per day). The 50% relationship was chosen as a conservative estimate since the laboratory dicromate and permanganate COD test measures more carbonaceous BOD than can occur through biological means. The

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BOD for the holding tank sample was used to represent that expected from the water-based wastewater. The BOD for the booth 3 sample was used to represent that expected from the solvent-based wastewater. The BOD for the recycle sample was used to represent that expected from the alum treated solvent-based wastewater. The existing and design BOD loads for the treatment plant were taken from the 1992 Chapter 94 Municipal Wasteload Management Report (Gwin, Dobson & Foreman, 1993). The ammonia nitrogen ($\text{NH}_3\text{-N}$) load was calculated using values determined through laboratory analysis (multiplying the flow by the concentration of $\text{NH}_3\text{-N}$ and converting to pounds per day). The $\text{NH}_3\text{-N}$ for the holding tank sample was used to represent that expected from the water-based wastewater. The $\text{NH}_3\text{-N}$ for the booth 3 sample was used to represent that expected from the solvent-based wastewater. The $\text{NH}_3\text{-N}$ for the recycle sample was used to represent that expected from the alum treated solvent-based wastewater. As ammonia is not yet a reportable parameter under the Saxton POTW's NPDES, no existing or design $\text{NH}_3\text{-N}$ loads were available from operator records or the 1992 Chapter 94 Municipal Wasteload Management Report (Gwin, Dobson & Foreman, 1993). An existing ammonia concentration for the treatment plant was conservatively assumed to have a concentration of 30 mg/L (Viessman and Hammer, 1993, p. 532). The estimate of sludge generation was made assuming 50% of the SS load, 40% of the BOD load and 20% of the $\text{NH}_3\text{-N}$ load will go to sludge.

The "Monthly-Discharge" situation (upper section of Table 4.2.1) was constructed using data from samples taken from unit processes in which the wastewater had been recirculating for 36 days (The Seton Company's Saxton plant operates 7 days/week). This table represents the loads expected if the Seton Company was to discharge its

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concentrated recirculatory wastewaters to the Saxton plant essentially once a month on one particular day.

The "Daily-Discharge" situation (center section of Table 4.2.1) was constructed using the same data, but dividing the results by 36 working days (assuming the concentrations to be cumulative). This table represents the loads expected if the Seton Company was to discharge its wastewaters to the Saxton POTW on a daily basis rather than allow the wastewaters to be recirculated and become more concentrated.

The "Weekly Discharge" situation (lower section of Table 4.2.1) was constructed using the same data, but dividing the results by 5 weeks (36 working days). This table represents the loads expected if the Seton Company was to recirculate its wastewaters for one week and then discharge those wastewaters to the Saxton POTW on one particular day of that week.

4.3 Aerobic Respirometer Tests

Results of the aerobic respirometer tests are provided in Figure 4.3.1 and Figure 4.3.2. The graphs depict the results of tests on 1 ml samples of each wastewater. The samples were added to the 250 ml aerobic respirometer bottles along with NMB medium, phosphate buffer, 2-chloro-6-trichloromethyl pyridine (TCMP) nitrification inhibitor, 10 ml of seed microorganisms from the MCR and sufficient distilled water to dilute the contents to 250 ml volume. A 30 percent potassium hydroxide (KOH) off-gas (CO_2) scrubber device and stir rod were carefully inserted into the bottles. The serum bottles were then sealed with rubber septum caps and connected to the Challenge AER-200 Aerobic Respirometer apparatus. The test was allowed to run for 13 days. Data was automatically collected every 2 hours. The data was seed corrected by subtracting the seed data from the data obtained from the control sample (50 ml of seed) after the control

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seed data was normalized to the 10 ml amount used in the test samples. The data was then adjusted for dilution effect by dividing the data by the amount of sample used, in this case, 1 ml or 0.001 liter. The data was then plotted as oxygen uptake versus time. The following formula was used in the determination of the data (Young, 1992):

$$C = [A - B (S_A / S_B)] \times [1000 / N_A]$$

where,

C = Corrected oxygen uptake [mg/L]

A = Measured oxygen in sample A [mg]

B = Measured oxygen in seed sample B [mg]

S_A = Amount of seed in sample A [ml]

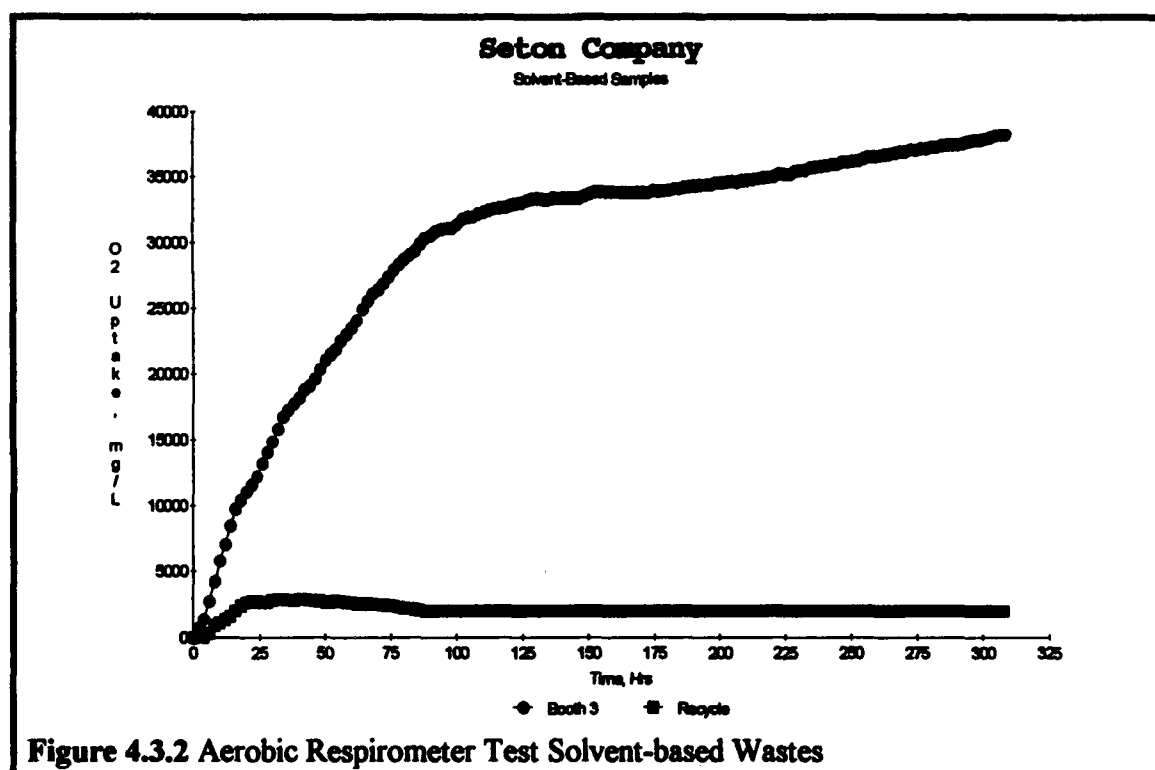
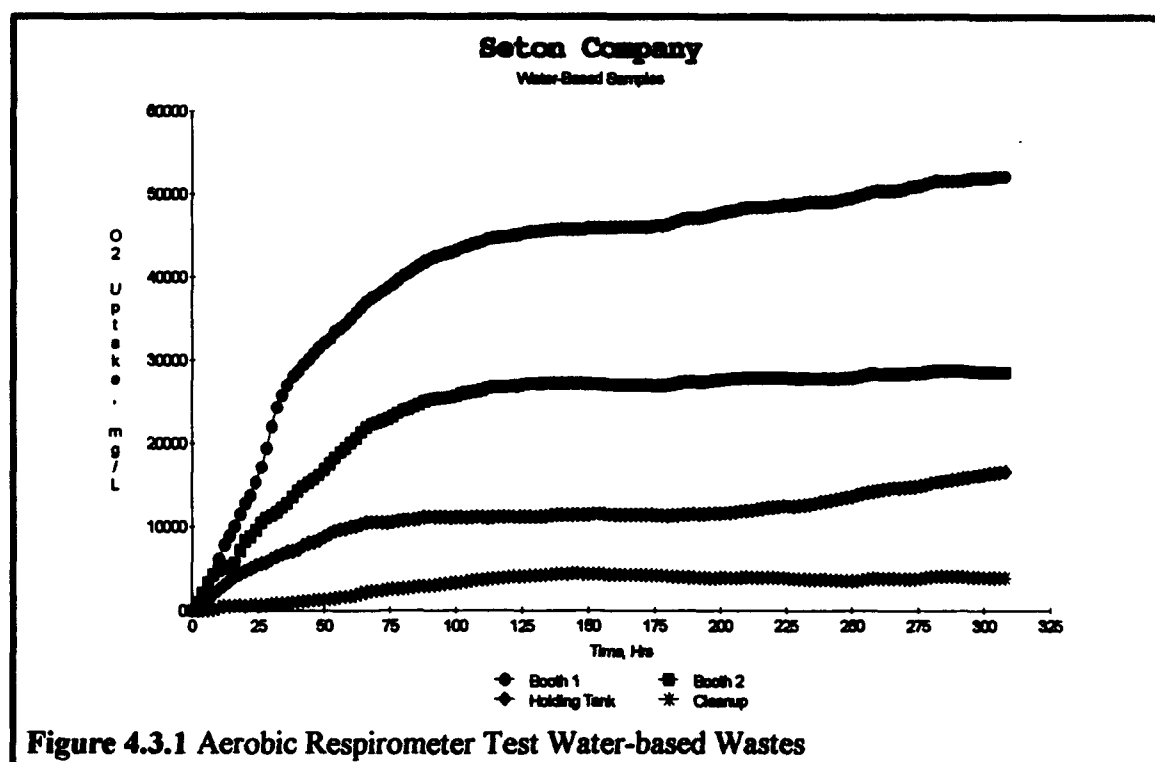
S_B = Amount of seed in sample B [ml]

N_A = Amount of undiluted test sample in sample A [ml]

4.4 Nonrecirculated Sample Analysis

To validate the assumption that the recirculated wastewaters experience a cumulative concentration effect, additional samples were obtained from the Seton Company's Saxton plant representative of one-day run concentrations. The samples were taken from each of the operating process booths one day after the water in each booth had been exchanged with fresh water. Table 4.4.1 shows the resultant characteristics measured for each sample. Again, booths 1, 2 and 4 are water-based paint effluents, while booth 3 possesses solvent-based coatings wastewater.

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SAMPLE	pH	TSS mg/L	VSS mg/L	TS mg/L	VS mg/L	SCOD mg/L	TCOD mg/L	TKN mg/L	NH3-N mg/L
Booth 1 (Water-based)	8.89	634	358	3020	1650	6300	9900	210	181
Booth 2 (Water-based)	7.06	499	436	2930	2260	3900	5500	203	85
Booth 3 (Solvent-based)	7.02	590	312	62330	16100	33700	34600	2820	1010
Booth 4 (Water-based)	6.89	1180	652	76880	21580	37700	39600	3630	840
Cleanup (Washbay)	8.64	8800	5400	15180	9840	21000	31500	420	158

Table 4.4.1 Characterization of Nonrecirculated Waste Effluent Samples After 1 day of Operation

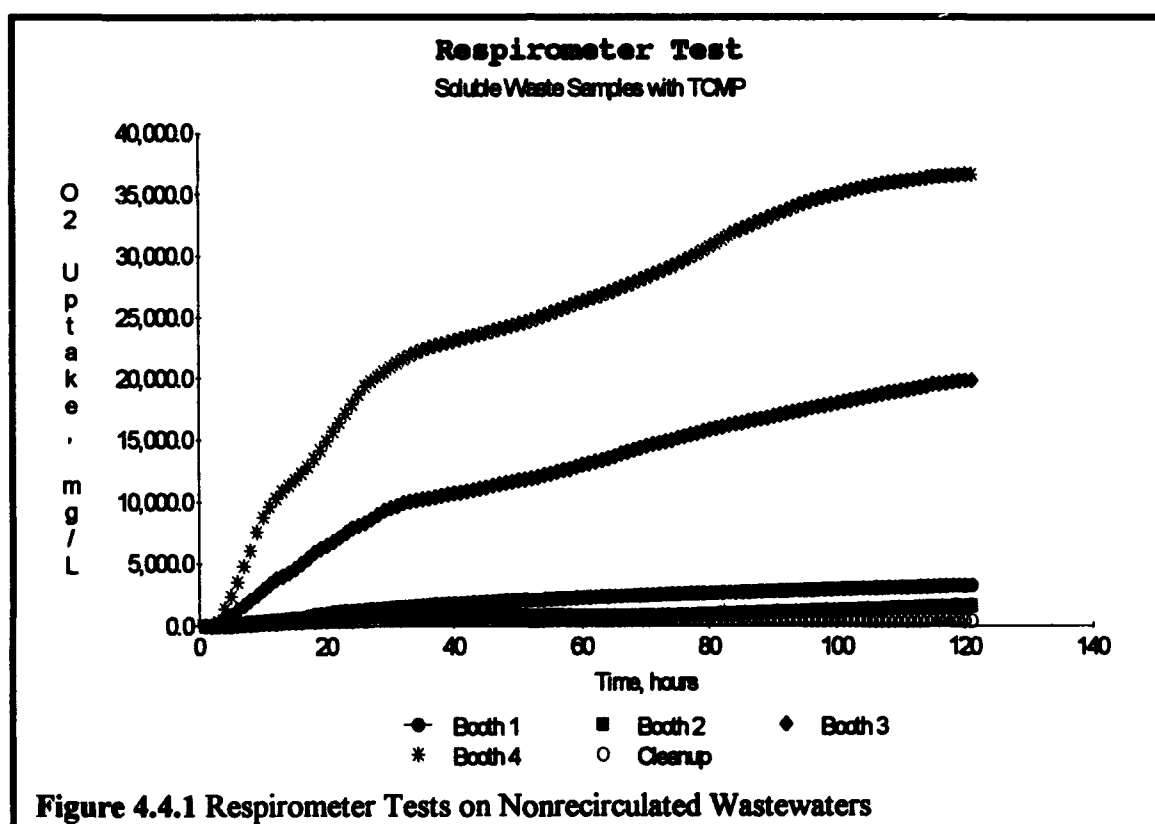
BEST CASE - DAILY SITUATION					
OPTIONS	FLOW gpd	SS Load lb/day	BOD Load lb/day	NH3-N Load lb/day	EST. SLUDGE Load lb/day
Water-Based Effluent					
Booths 1,2,4 & Wash Bay	3500	59	197	10	110
Booths 1,2,4,5,6 & Wash Bay	6000	112	367	18	206
Solvent-Based Effluent					
Booth 3 w/o removal	1000	5	97	8	43
Booths 3 & 7 w/o removal	2000	10	194	17	86
Totals					
Existing Ops w/o removal	4500	64	294	18	153
Future Ops w/o removal	8000	122	561	35	292
Other					
Saxton POTW Existing Load	207000	226	326	60	256
Saxton POTW Design Load	400000	684	587	***	577

Table 4.4.2 Mass Balance Analysis of Nonrecirculated Wastewaters

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Using the data of Table 4.4.1, a mass balance analysis was again accomplished. Table 4.4.2 depicts the results of the mass balance analysis assuming the nonrecirculated wastewater is discharged on a daily basis.

Additional aerobic respirometer tests were run on the nonrecirculated samples to assess any differences. The resulting graphs of the respirometry data are depicted in Figure 4.4.1. In an effort to assess the effects of nitrogenous BOD, additional aerobic respirometer tests were conducted on the nonrecirculated samples by neglecting to add the nitrogen inhibiting compound TCMP. These results are depicted in Figure 4.4.2.



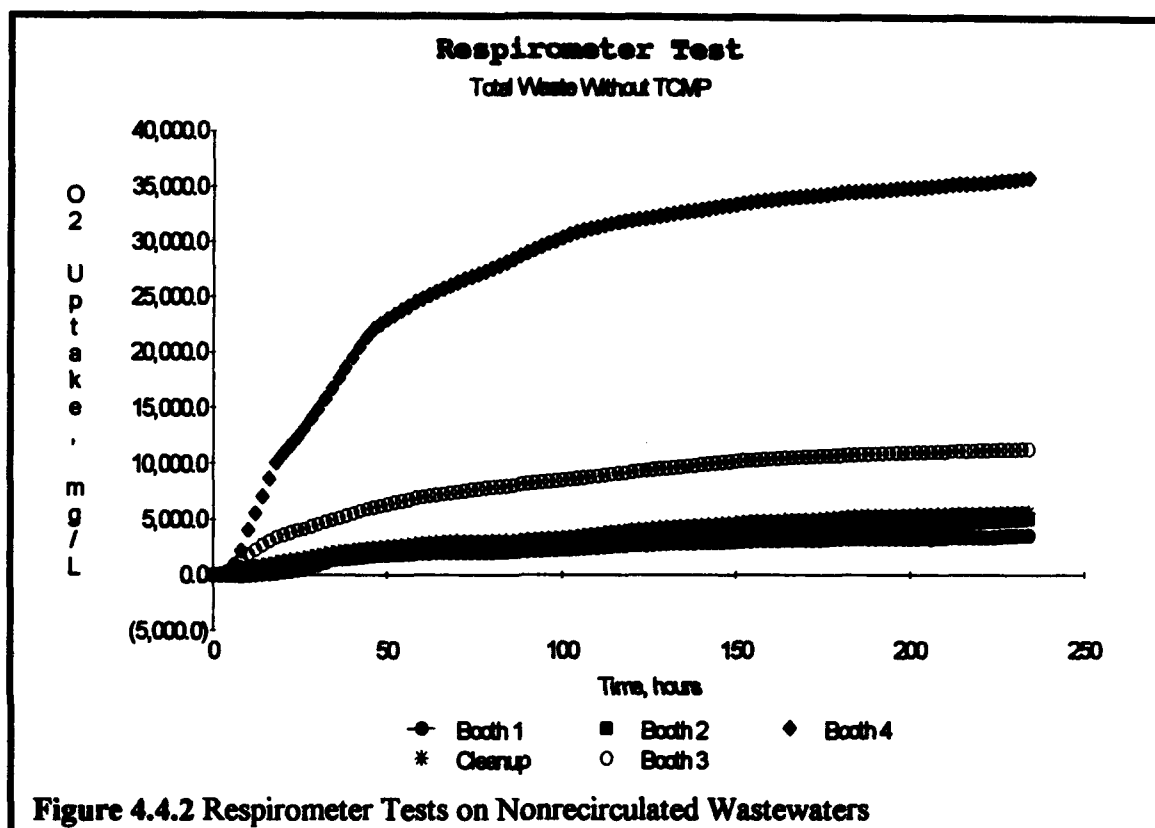
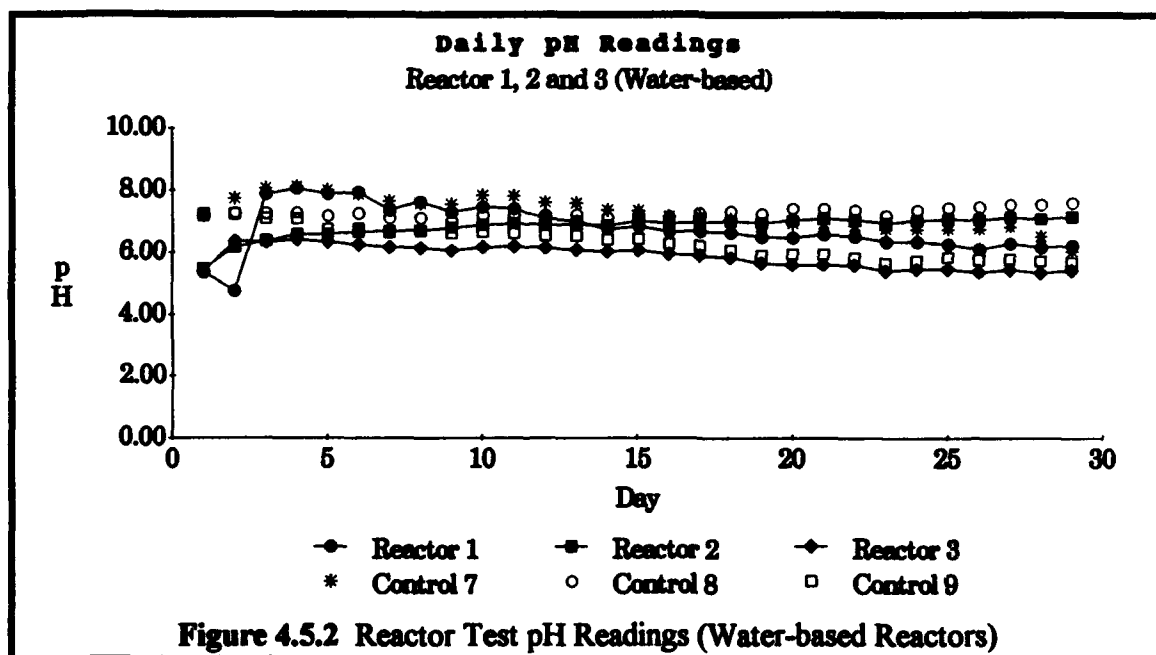
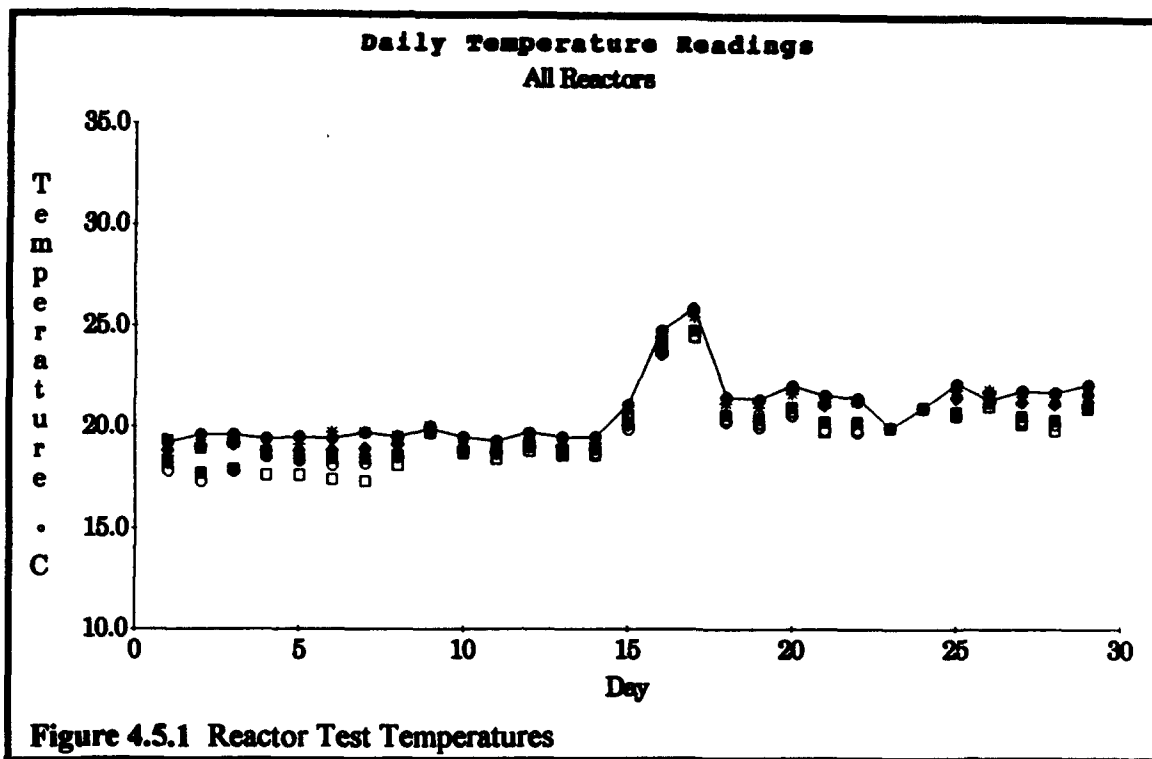


Figure 4.4.2 Respirometer Tests on Nonrecirculated Wastewaters

4.5 Bench-scale Reactor Tests

Figure 4.5.1 depicts the average temperatures of the reactors as measured daily. The test temperature remained fairly constant except for a peak at days 15-17. This peak was due to a break down of the building's air conditioning system. Figures 4.5.2 and 4.5.3 depict the daily pH measurements from each reactor compared to that of the control reactors.



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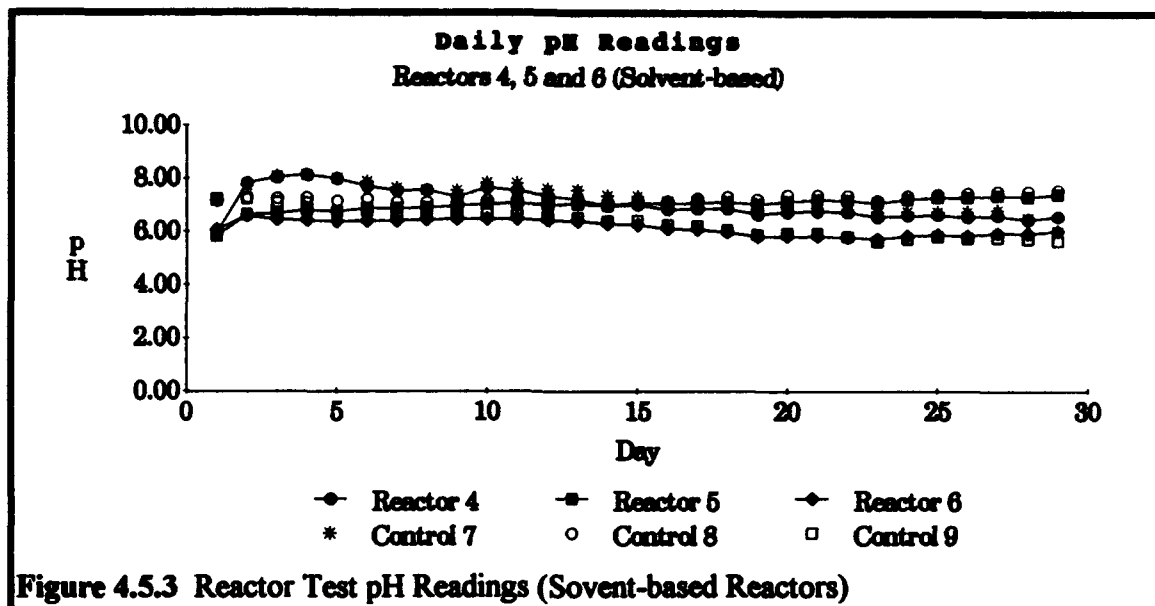
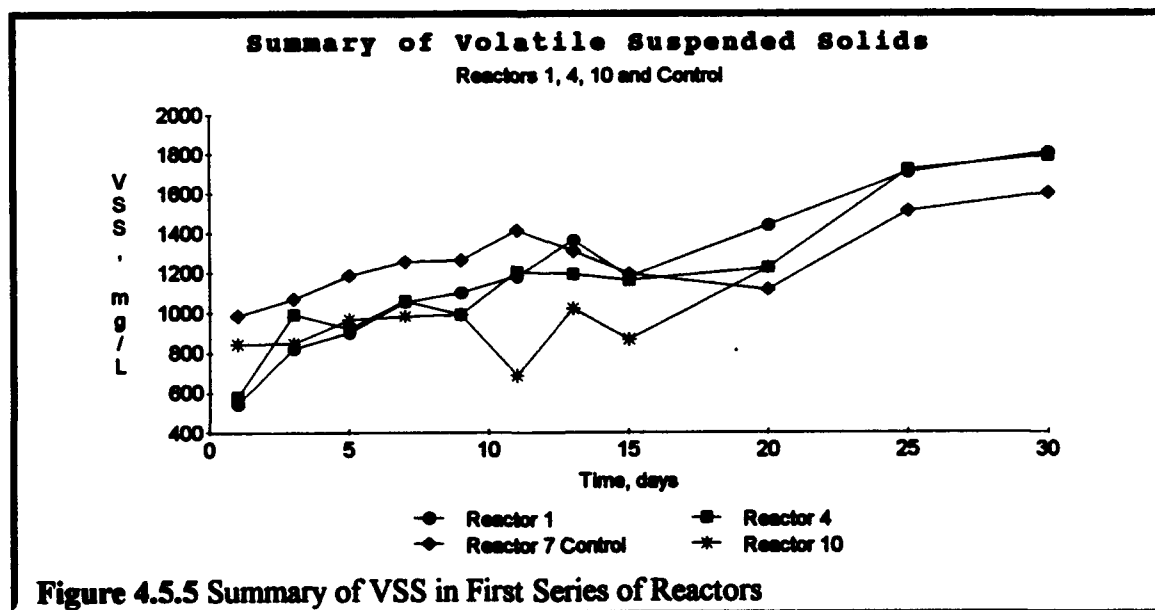
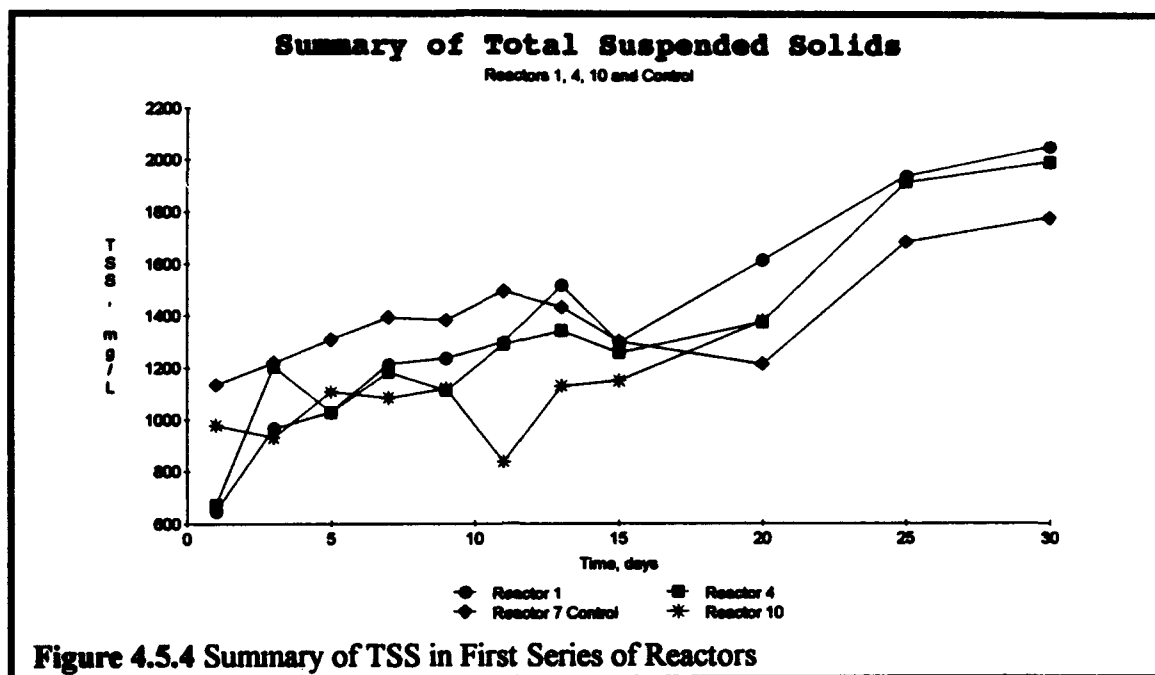


Figure 4.5.4 summarizes the total suspended solids of the first series of reactors. This first series of reactors received the raw waste feeds of ethanol base, water-based waste, or solvent-based waste. The feed stock was added at a loading rate of 1 gram of COD material per liter per day. The amount of raw waste (solvent or water-based) in the feedstock mixture was a percentage of what the Saxton POTW would expect to see if the Seton Company was to discharge that particular waste on a daily basis according to their current operating volumes. Appendix C provides a detailed explanation of the feedstock calculations. Also included in Figure 4.5.4 is the results of a tenth reactor which was started midway through the testing period. This reactor was fed a combination of wastes (solvent and water-based) at the same loading rate, but was operated at an SRT of 5 days. Figure 4.5.5 summarizes the VSS of this first series of reactors. Using the data from Figures 4.5.4 and 4.5.5 a summary of the percent of VSS was constructed and is depicted in Figure 4.5.6.



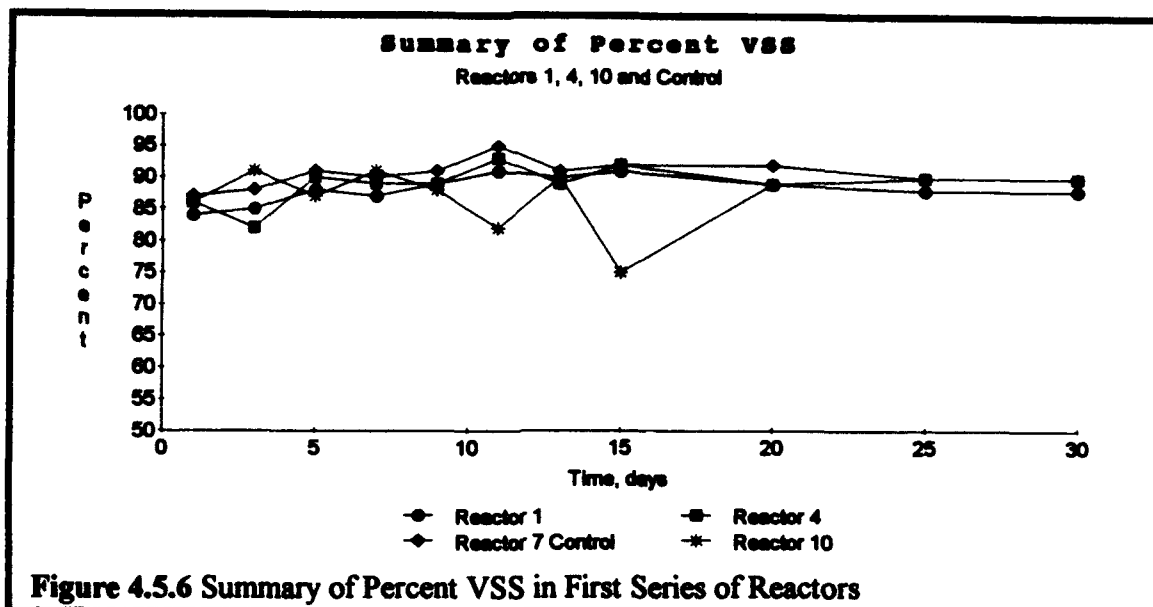
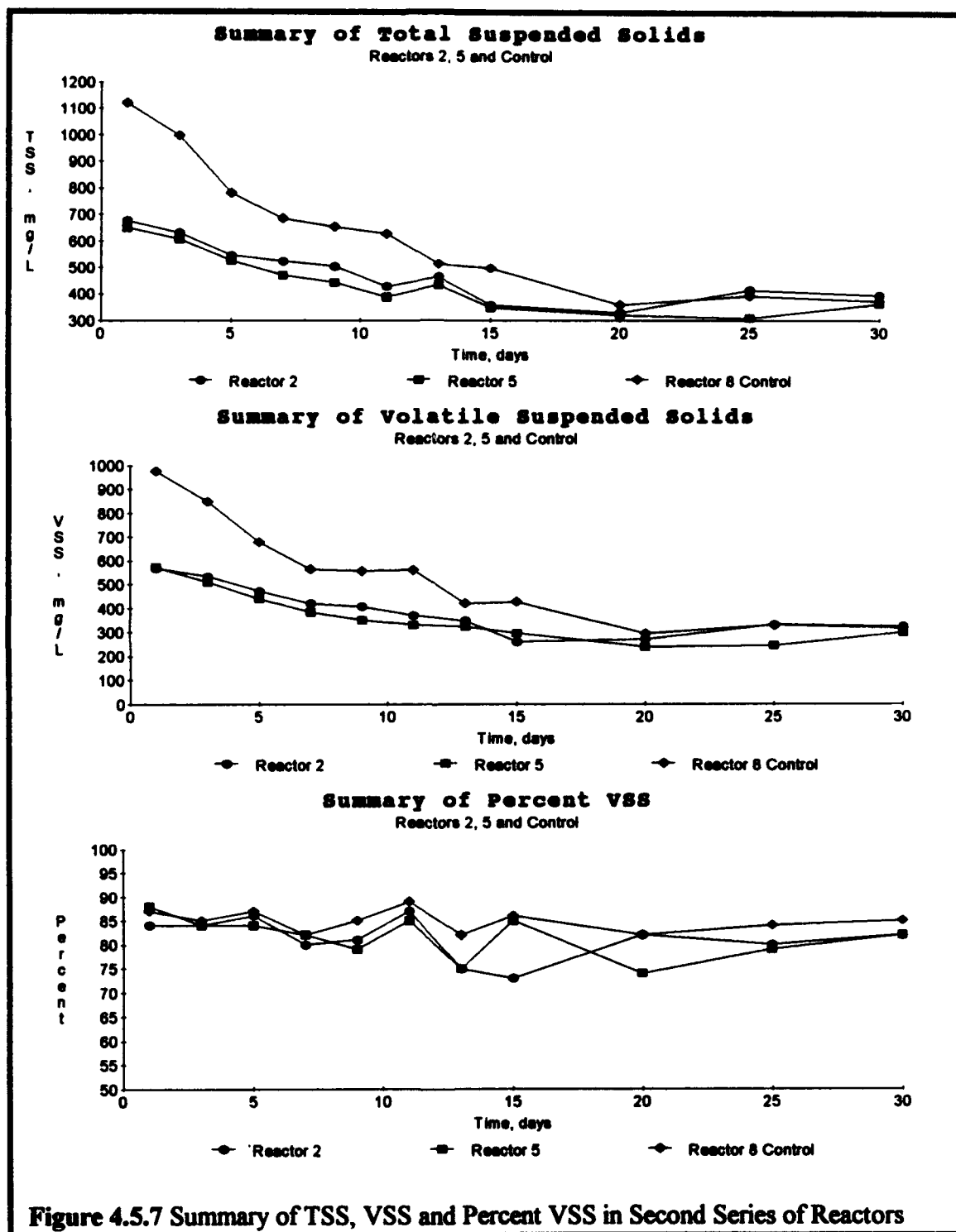


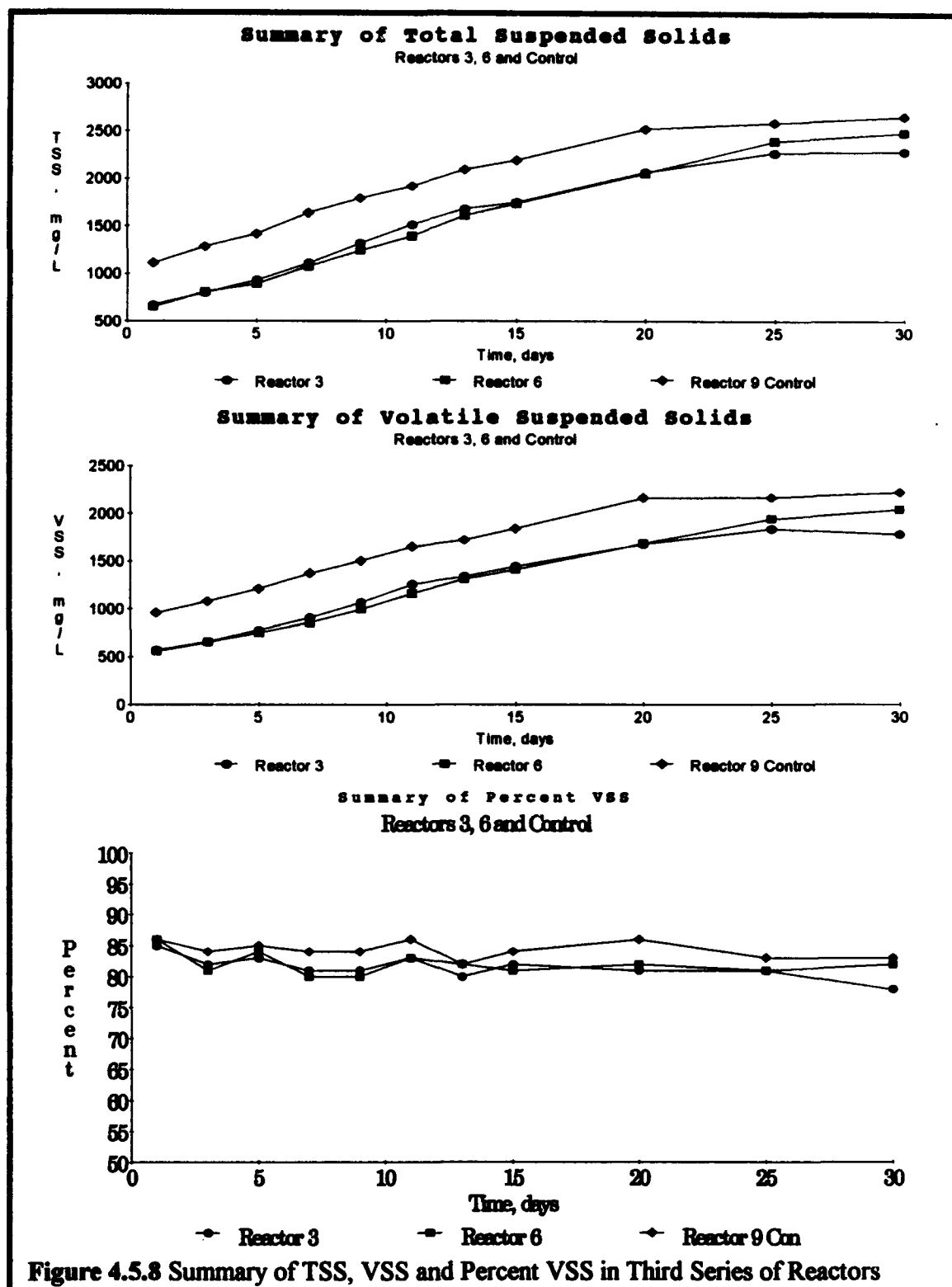
Figure 4.5.7 summarizes the same data for the second series of reactors. These reactors were fed the effluent of the first series of reactors. The loading rate depended upon the degree of decomposition occurring in the first reactors.

Figure 4.5.8 summarizes the same data for the third series of reactors. These reactors were fed the sludge solids of the first and second series of reactors. The loading rate depended upon the degree of decomposition occurring in the first and second reactors.

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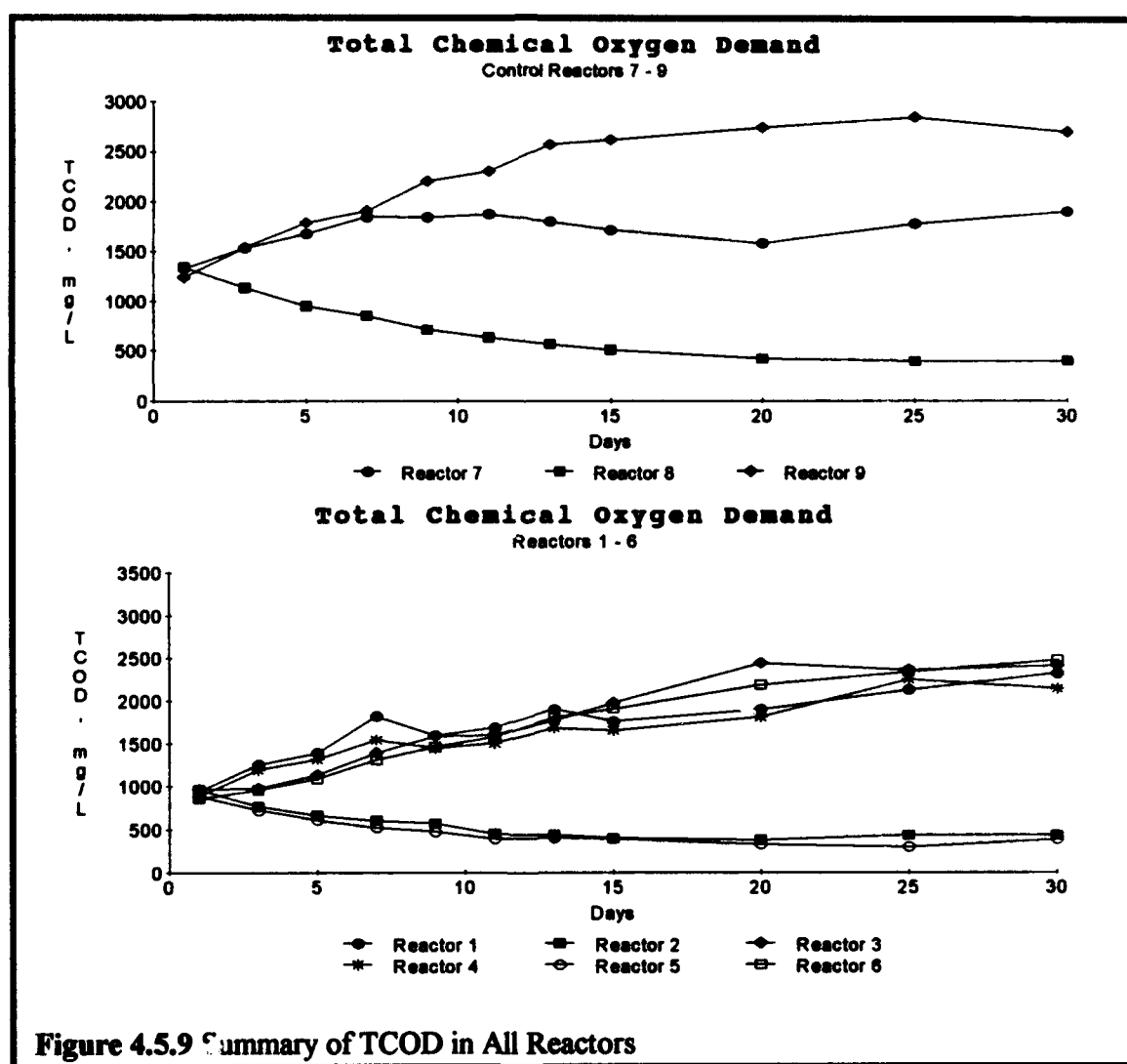


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Figure 4.5.9 summarizes the results obtained from TCOD tests run on samples from each reactor. The top graph depicts the results measured in the control reactors, while the lower graph depicts those measured in the water-based and solvent-based reactors.



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Figure 4.5.10 summarizes the results obtained from SCOD tests run on samples from each reactor. The top graph depicts the results measured in the control reactors, while the lower graph depicts those measured in the water-based and solvent-based reactors.

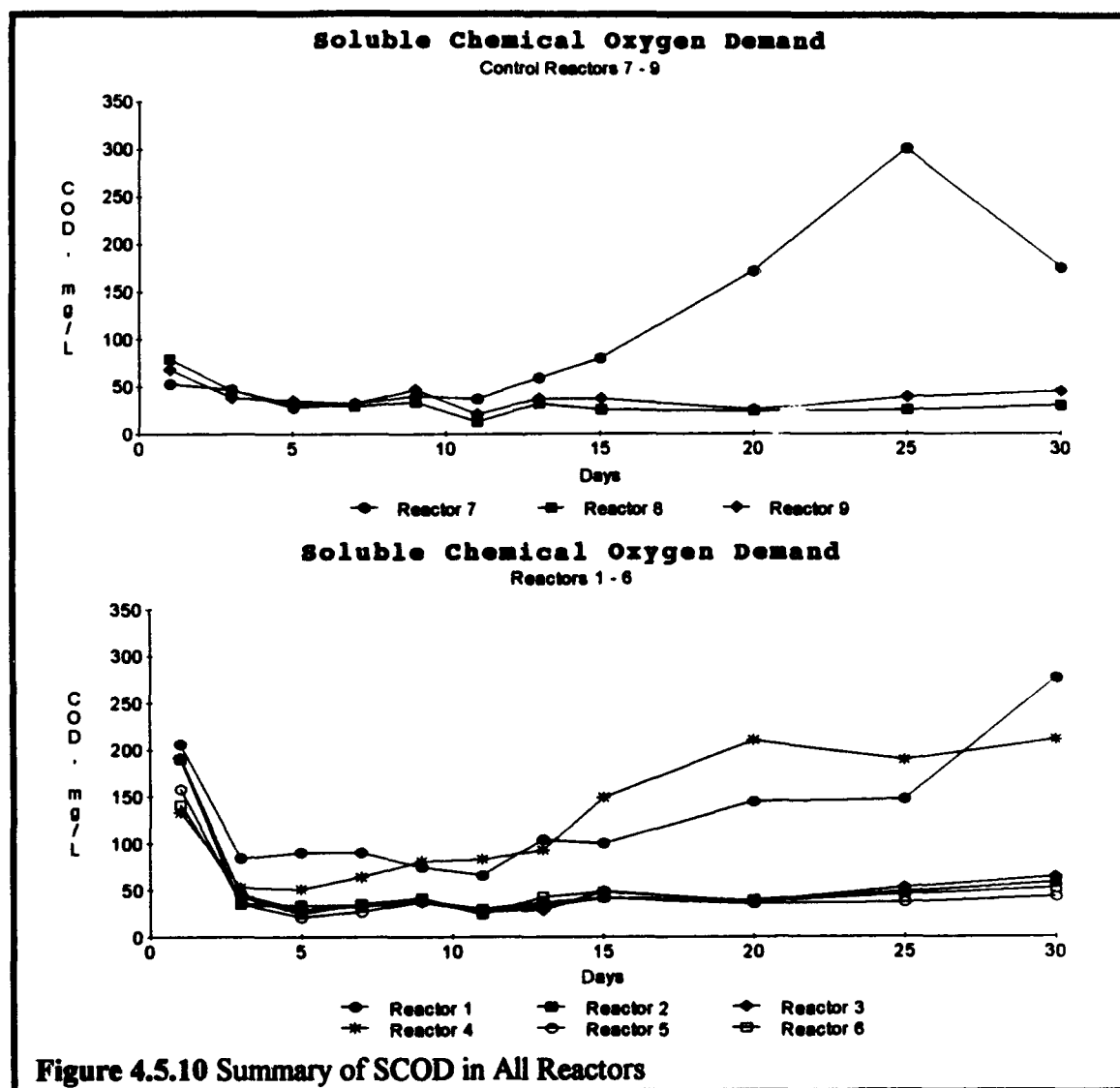
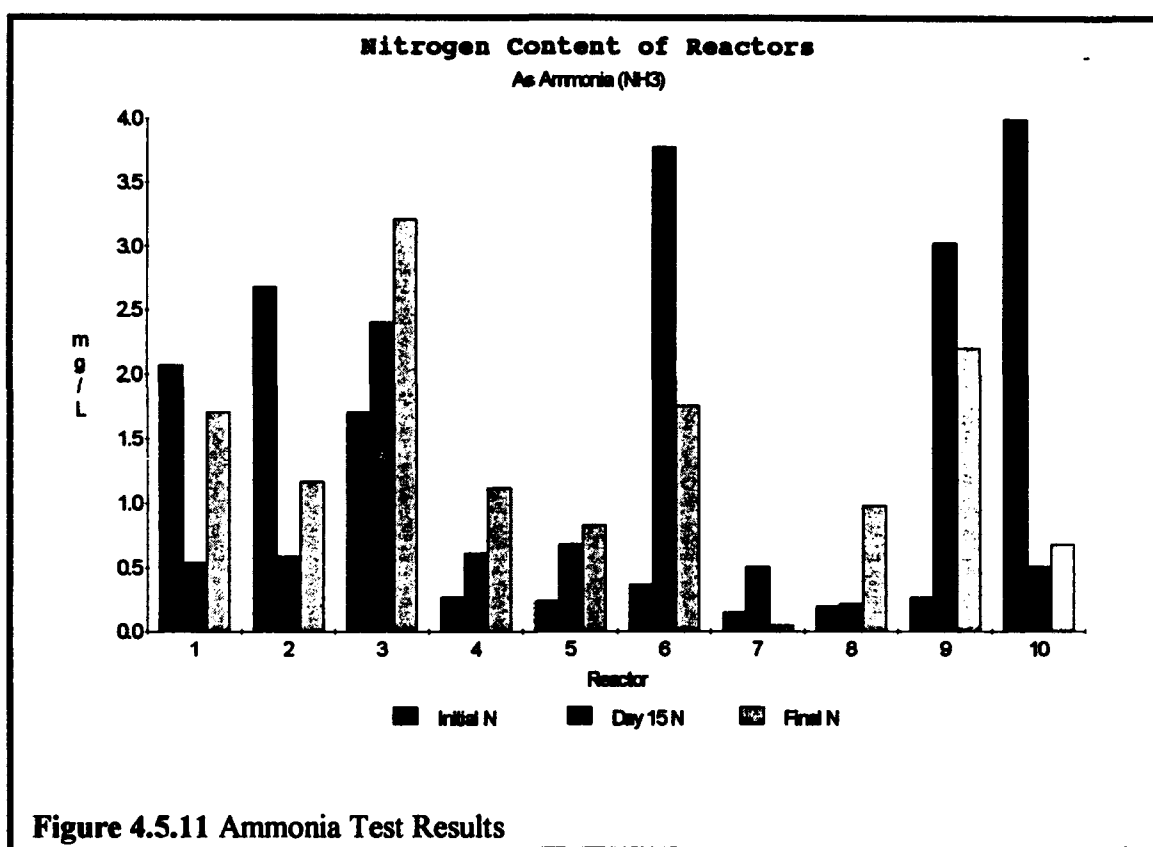


Figure 4.5.11 depicts the results obtained in tests for nitrogen content of the reactors. It should be noted that the nitrogen content, as ammonia, of the initial activated

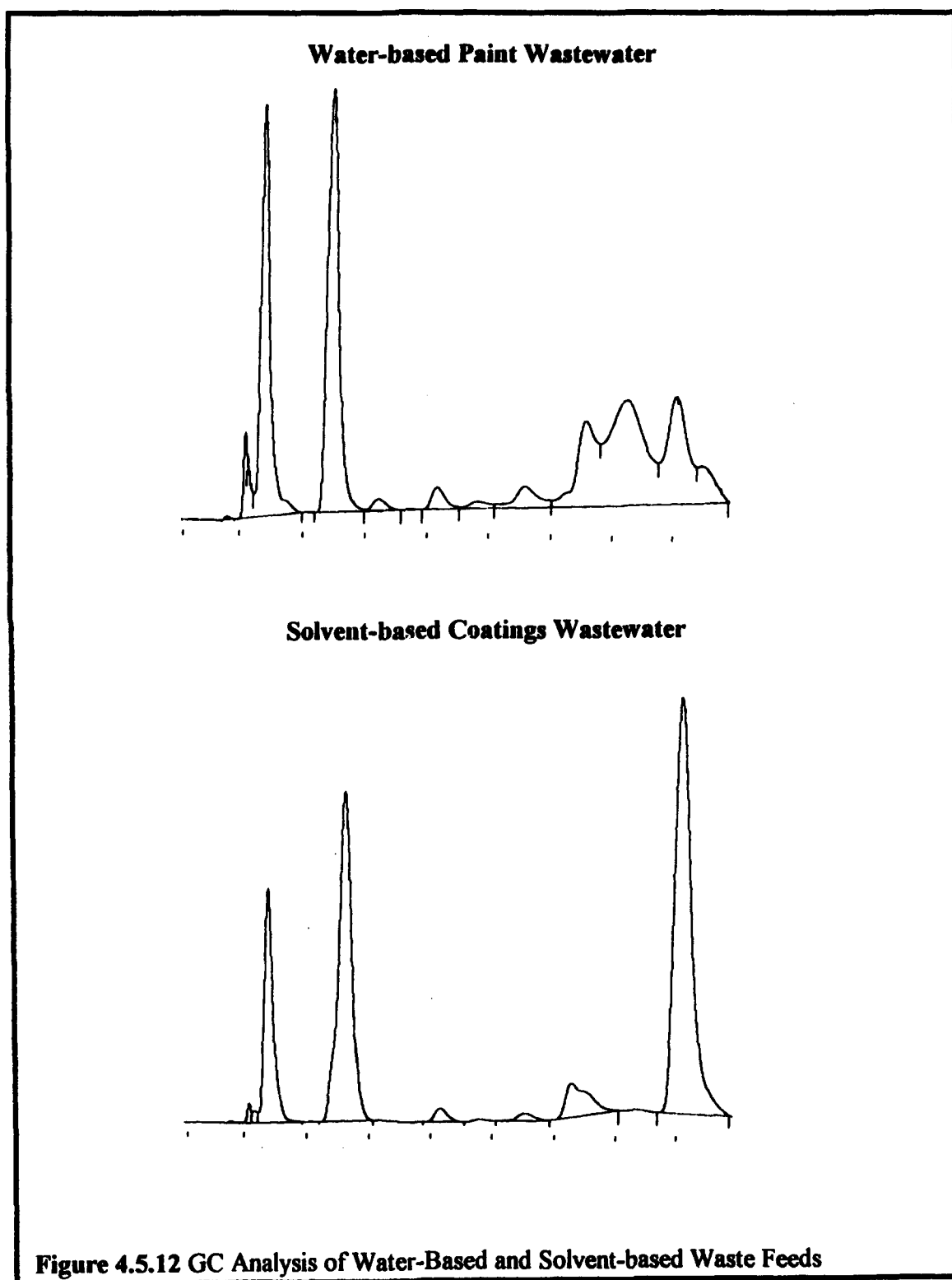
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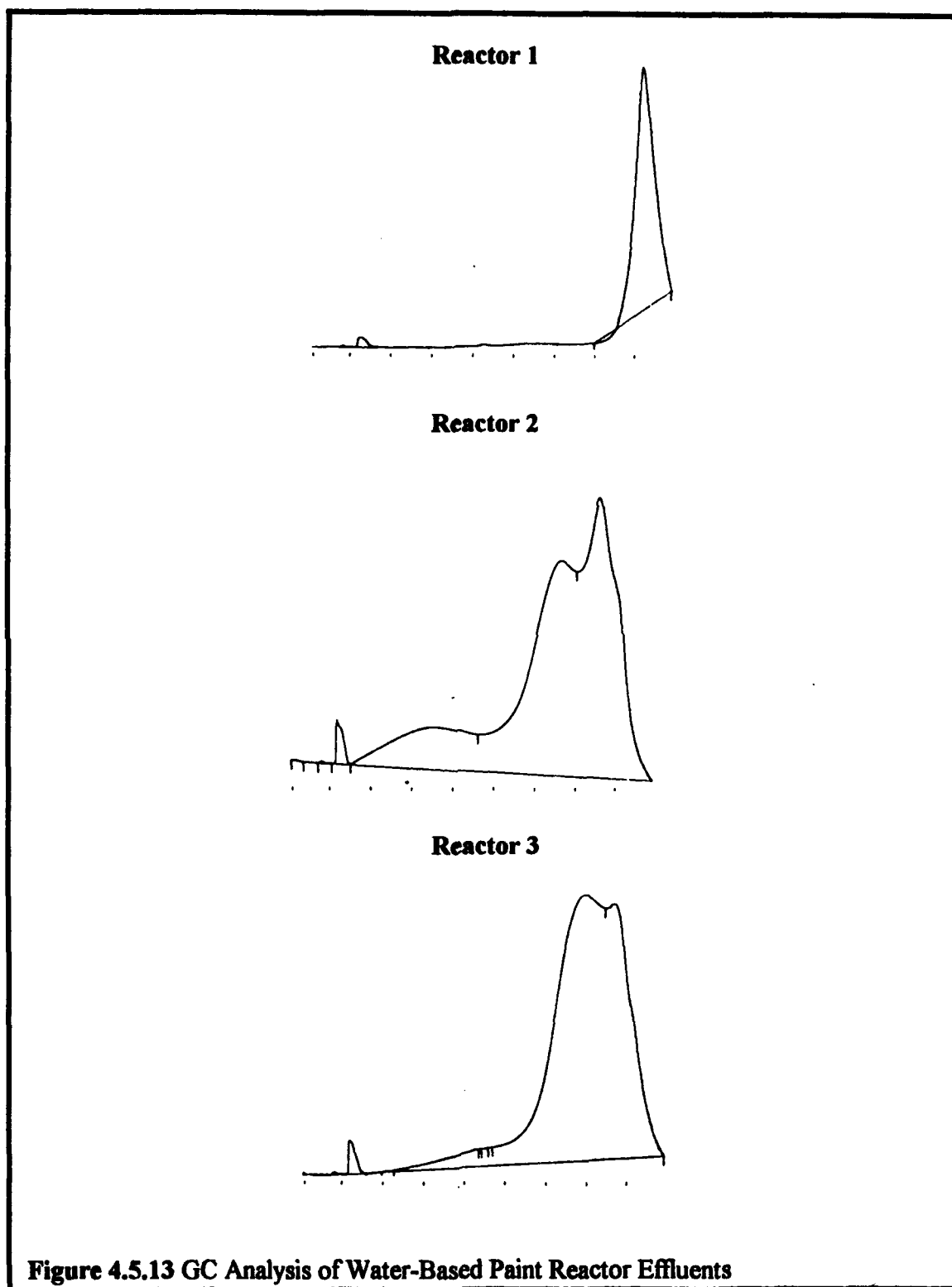
sludge was 41.2 mg/L. This is the value measured for the initial reading of reactor 10. The value shown for the initial reading of reactor 10 (only) in the graphs was changed to tenth scale in order to make the information easier to read. The lower initial values for the other reactors is most likely due to the fact that the test was restarted after 10 days and the activated sludge was simply remixed rather than replaced with fresh.

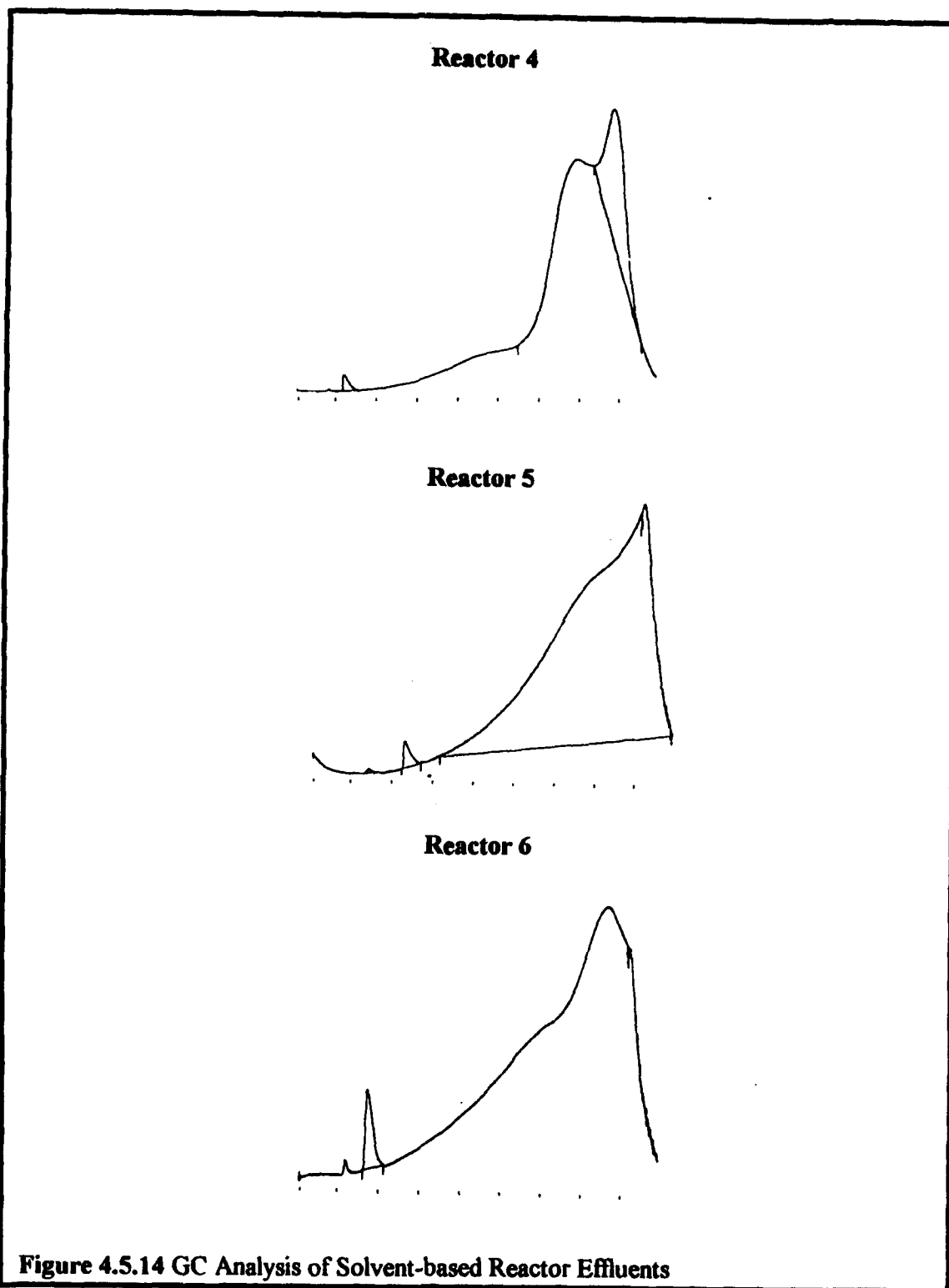


Samples of effluent were collected both initially and immediately following the 30 days of testing for each reactor. These samples were analyzed using GC methods. Figures 4.5.12, 4.5.13 and 4.5.14 show the results of a comparative analysis of the compounds found in the listed samples.

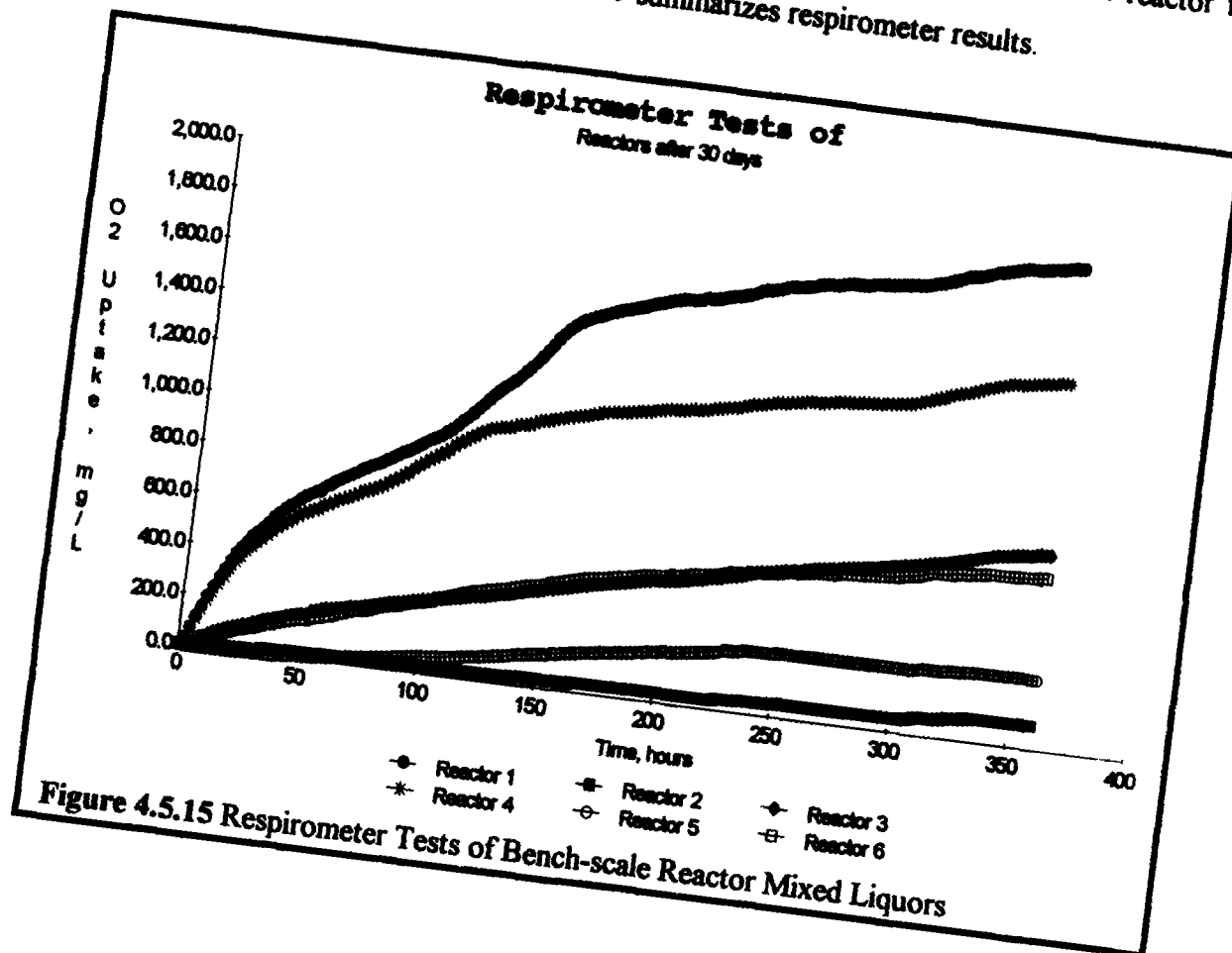
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Respirometer tests were run on the mixed liquors generated by each reactor to assess the oxygen uptake. Figure 4.5.15 summarizes respirometer results.



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Discussion

5.1 Aerobic Treatability

Results obtained in Phase I aerobic respirometer tests indicate that all of the recirculated wastewater samples taken from the Seton Company's Saxton plant are aerobically biodegradable, to some limited extent. Using the amount of oxygen uptake ultimately achieved during the respirometer run on the raw waste samples and dividing by the TCOD of the compound gives an estimate of the biodegradability measured in the tests. Table 5.1.1 lists the estimated degree of biodegradability determined for each sample. The numbers expressed however, do not necessarily indicate poor biodegradability, rather they indicate the amount of ultimate aerobic biodegradation to by-products of carbon dioxide, water and cellular mass. The remaining compounds may have

<u>SAMPLE</u>	<u>BIODEGRADABILITY</u>
Recycle	28%
Cleanup	10%
Booth 3	48%
Booth 2	40%
Booth 1	22%
Holding Tank	7%

Table 5.1.1 Degree of Biodegradability of Recirculated Wastewater Samples

been changed to compounds readily utilized by other microorganisms not readily available in the test culture. Such may be the case as evidenced by the gradual rise in oxygen uptake in all but two of the samples after approximately 7 days of incubation (acclimation period). The results of the aerobic respirometer tests on the water-based paint wastes shown in Figure 4.3.1 indicated that the booth 1 waste has the highest oxygen demand. The cleanup wastewater sample had the lowest oxygen demand. It is interesting to note that the holding tank sample, which is a combination of booth 1, booth 2, and cleanup

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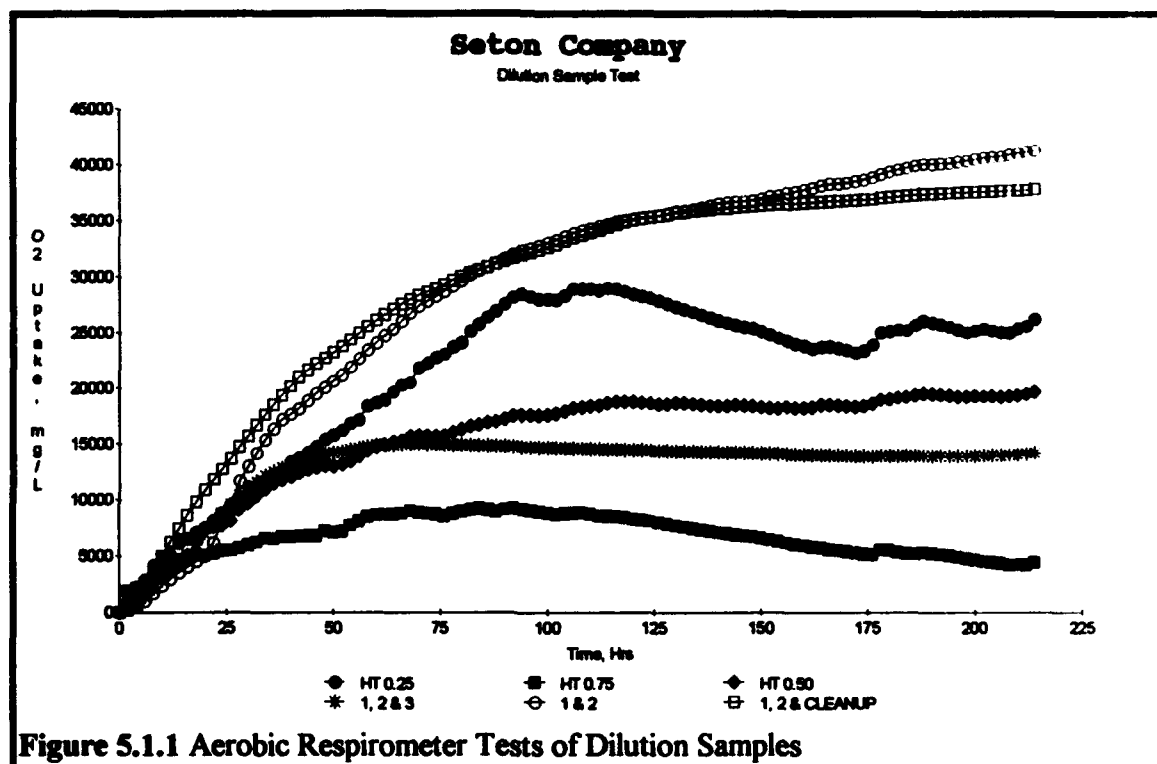
wastewater, had a much lower oxygen uptake than either booth 1 or booth 2 posing several possibilities. First, that the cleanup water was somehow inhibiting the biological activity of wastewaters from booth 1 and booth 2. Second, as the gradual rise after 7 days of testing indicated, perhaps a period of acclimation was necessary. Third, perhaps the combination of different compounds caused an inhibitory effect. Or, perhaps the majority of the water in the holding tank was actually cleanup water causing a dilution effect. It was originally assumed that the holding tank only held 1000 gallons from booth 1, 1000 gallons from booth 2, and 500 gallons from cleanup. If, however, 500 gallons of cleanup water was generated each day, then the amount accumulated in the holding tank after the 36 day period when sampled was actually 18,000 gallons, or 90 percent of the volume. Discussions with Seton Company officials indicated that this was indeed the case. The cleanup water is stored in a separate tank, but can also be transferred to the holding tank which has a volume of 4,340 gallons. Currently, the booth waters are recirculated as long as possible, but cleanup water is generated on a daily basis, and the total volume depends on process schedules and color changes. Thus, on a monthly discharge basis, the majority of the wastewater is actually cleanup water rather than process water. As Figure 4.3.1 and Table 5.1.1 indicate, there was very little degradation activity in the cleanup and holding tank samples. Since the holding tank was assumed to be a combination of booths 1, 2 and cleanup wastewaters it was assumed that the low activity of the holding tank sample was caused by the cleanup wastewater. Discussions with Seton Company officials regarding the cleanup wastewater process identified the use of an industrial cleaner "Bio-Might 100". According to the Material Safety Data Sheet (MSDS), this industrial cleaner is a non-toxic sodium silicate solution. Soluble silicates, such as sodium silicate are often used for waste solidification and coagulation aids. The chemical mechanism by which the

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activated silica operates is not known with certainty (Manahan, 1991). Silicates are essentially derived from weak acid treated silica compounds. Silica is essentially inorganic quartz, opal, or sand. It is possible that through some chemical mechanism the industrial cleaner may be binding up much of the organics needed by the microorganisms used in this study. Additional aerobic respirometer tests on varying dilutions of the holding tank wastewater and different combinations of the booth 1, booth 2 and cleanup wastewater were accomplished to determine which wastewater was causing the inhibition. Figure 5.1.1 depicts the results of the additional respirometer tests. Three different dilutions were run on the holding tank sample (represented as 0.25 ml, 0.50 ml, and 0.75 ml). It can be seen from the graphs of these samples that there is an inhibiting effect as the concentration of the holding tank sample is increased. Tests run on samples composed of a combination of wastewaters are also depicted on the same graph. The results for a sample containing booth 1, 2 and cleanup wastewater yielded nearly the same results as a sample containing just booth 1 and 2 wastewater. These results imply that the original assumption that the cleanup water may be causing the inhibition may not be valid. An additional sample containing booth 1, 2 and 3 was also tested. The results, as shown on the same graph are very similar to the results obtained on the holding tank sample leading to further speculation that booth 3 wastewater may somehow be entering the holding tank and causing the inhibition. This could occur if the stainless steel mixing tanks used for the solvent-based booth 3 are washed in the same washbay as the mixing tanks used for the water-based booths. The degree of biodegradation for the samples depicted in Figure 5.1.1 was determined and the results are listed in Table 5.1.2. Table 5.1.2 shows that the mixing of booth 3 solvent-based wastes to the water-based paint waste stream decreases the degree of biodegradability of the wastewater (from 35% to 14%), whereas the mixing

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of cleanup water with the water-based paint waste stream showed an increased degree of biodegradability (from 35% to 39%).



SAMPLE

BIODEGRADABILITY

Holding Tank 0.25 ml	19%
Holding Tank 0.50 ml	13%
Holding Tank 0.75 ml	6%
Booth 1 and 2	35%
Booth 1, 2 and 3	14%
Booth 1, 2 and Cleanup	39%

Table 5.1.2 Degree of Biodegradability of Diluted and Mixed Wastewater Samples

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5.2 Effects on Wastewater Treatment Plant

The results of the flow analysis shows only a limited effect on the average wastewater flow to the Saxton POTW in either discharge situation. The anticipated 4500 gallons/day of wastewater discharge under current operations or the anticipated 8000 gallons/day of wastewater discharge under the expanded operations will have only a limited impact on the average wastewater flow of 200,000 gallons per day the POTW currently experiences. The Saxton POTW has experienced several peak flows beyond their permitted discharge limit. Analysis of these events showed they occurred during periods of heavy rainfall indicating infiltration of sewers by the runoff. During these periods any additional loading on the plant will exacerbate the peak flow problem.

The results of the mass balance analysis (Figure 1.3.3) using the recirculated sample data shows that discharge under the current Seton Company practice of wastewater recirculation for about 30 days with one day a month disposal, the loads on the plant (SS, BOD, $\text{NH}_3\text{-N}$, sludge) would be far greater than the Saxton POTW was originally designed to handle. Figure 1.3.3 also shows that weekly recirculation and discharge would cause the Saxton Treatment Plant to operate on the upper boundary of its designed capabilities during that particular day of discharge. The mass balance results of Figure 1.3.3 show that a daily discharge of wastewaters to the Saxton POTW will have the least adverse effect of all other discharge situations. Daily replacement of water in each booth will provide a diluted wastewater to the treatment plant. The overall effect as shown in the mass balance analysis (Table 4.2.1) is a 2% increase in hydraulic flow, a 15 percent increase in SS load, 10% increase in BOD load, and 4% increase in ammonia load to the Saxton POTW under current operations. Under expanded operations, mass balance analysis shows a 4% increase in hydraulic flow, a 27% increase in SS load, a 17% increase

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in BOD load, and a 6% increase in ammonia load. Even with the increase in loading for expanded operation, the Saxton POTW will operate at only 54% of the design flow load capacity, 42% of the design SS load capacity, and 65% of the BOD design load capacity. Daily discharge and replacement of water in each booth however, will increase the Seton Company's current annual water usage of 54,000 gallons by more than 30 times to 1,642,500 gallons. The increased cost of process water may surpass the current cost of wastewater disposal.

Validation of the original assumption that the recirculated wastewaters experience a cumulative concentration effect was accomplished by testing samples of one-day run concentrations. A direct comparison of the characterizing results previously shown in Table 4.2.2 (recirculated) and those shown in Table 4.4.1 (nonrecirculated) cannot be made as the results for the recirculated samples must first be divided by 36 (number of concentration days). Table 5.2.1 depicts the corrected data for recirculated and one-day concentration wastewaters. The cleanup wastewater sample was assumed to be a one-day concentration sample in both cases. The only factors that can be compared are those for booths 1, 2 and 3, as no samples were taken from the other areas. Comparing SS, the actual one-day concentration is less than originally assumed for booths 1 and 2 but much higher (63%) for booth 3. Comparison of COD shows the actual COD to be much greater (45% in booth 1, 68% in booth 2, and 95% in booth 3) in the one-day concentration samples than assumed. Comparing ammonia, the actual one-day concentration is greater (35% in booth 1, 53% in booth 2, and 89% in booth 3) in the one-day concentration samples than assumed. From these results, it is inappropriate to estimate loading on the Saxton POTW using the data measured on the recirculated wastewaters corrected for 36

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days of concentrated run time. Rather, estimates on loading should be made using the data measured on the nonrecirculated wastewaters.

<u>One-Day Concentration (mg/L)</u>							
<u>SAMPLE</u>	<u>pH</u>	<u>TSS</u>	<u>VSS</u>	<u>SCOD</u>	<u>TCOD</u>	<u>TKN</u>	<u>NH3-N</u>
Booth 1	8.89	634	358	6300	9900	210	181
Booth 2	7.06	499	436	3900	5500	203	85
Booth 3	7.02	590	312	33700	34600	2820	1010
Booth 4	6.89	1180	652	37700	39600	3630	840
Cleanup	8.64	8800	5400	21000	31500	420	158
<u>Recirculated Wastewater Corrected to Expected One-Day Concentration</u>							
<u>SAMPLE</u>	<u>pH</u>	<u>TSS</u>	<u>VSS</u>	<u>SCOD</u>	<u>TCOD</u>	<u>TKN</u>	<u>NH3-N</u>
Recycle	6.45	10	4	264	286	20	8
Cleanup	8.64	8800	5400	21000	31500	420	158
Booth 3	6.22	217	100	1806	1819	134	109
Booth 2	7.56	872	469	1361	1753	122	40
Booth 1	8.13	2097	1347	3361	5394	165	118
Holding Tank	8.90	1119	889	2708	4214	46	21

Table 5.2.1 Comparison of Recirculated and Nonrecirculated Wastewaters

Comparing the mass balance analysis using recirculated wastewater data (Table 4.2.1) to the mass balance analysis using nonrecirculated wastewater data (Table 4.4.2), shows that in all areas the loadings are actually greater than assumed (50% higher SS, 90% higher BOD, 90% higher ammonia, and 85% more sludge). As for the effect on the Saxton POTW, the average SS load on the treatment plant will increase 28% under Seton's current operations and 54% under Seton's future operations. Even with this future increase in SS load, the treatment plant will be operating at only 51% of its design load capacity. The ammonia load on the treatment plant will increase 30% under Seton's current operations and 58% under Seton's future operations. The BOD load on the

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treatment plant will increase 90% under Seton's current operations and 172% under Seton's future operations. With the increase in BOD load under current Seton operations, the treatment plant will be operating at 106% of its design load capacity. With the future increase in BOD load, the treatment plant will be operating at 151% of its design load capacity.

Results obtained from aerobic respirometer tests on nonrecirculated Seton wastewaters (Figures 4.4.1 and 4.4.2) correlated well with the tests conducted on the recirculated samples. Using the amount of oxygen uptake ultimately achieved during the respirometer runs on these nonrecirculated samples and dividing by the TCOD of the samples gives an estimate of the biodegradability of the wastewaters. Table 5.2.2 lists the estimated degree of biodegradability determined for each nonrecirculated sample. Booth 4 wastewater was not available for the original recirculated sample test, and was found to possess a significant degree of biodegradability. The other nonrecirculated samples, however, generated the same results as the original recirculated samples possessing only a limited degree of biodegradability.

SAMPLE	BIODEGRADABILITY
Booth 1	33%
Booth 2	29%
Booth 3	57%
Booth 4	92%
Cleanup	2%

Table 5.2.2 Degree of Biodegradability of Nonrecirculated Wastewater Samples

Results of the bench-scale reactor tests showed that both the solvent-based and water-based waste-fed reactors differed only slightly in comparison to the control reactors. Both temperature and pH actions of the waste-fed reactors mirrored the controls. The

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first series of reactors were meant to simulate the activated sludge units at the Saxton POTW operating in parallel. Total suspended solids for these waste-fed reactors grew at a slightly greater pace than the control. The MLVSS of the waste-fed reactors were beginning to level out or reach an equilibrium towards the end of the study, or around 2000 mg/L. The MLVSS for the control reactor was slightly lower, or around 1800 mg/L. Likewise, the volatile suspended solids for the waste-fed reactors grew at a slightly greater rate than in the control. The waste-fed reactors were approaching an equilibrium towards the end of the study, averaging about 1800 mg/L. The percent of volatile suspended solids for the waste-fed reactors mirrored that of the control remaining fairly stable and equilibrating at about 90 percent. This solids accumulation indicates that there may be some additional biomass generated by adding the solvent-based coatings and water-based wastes, but there is apparently no build-up of inorganic fractions of waste.

The purpose of using the second series of reactors was to assess the impact of changing current POTW activated sludge parallel operations to series operations. Results indicated that the total suspended solids in the second series of reactors decreased at a rate similar to that in the control. Sufficient substrate was being received from the first series of reactors, however, to prevent a complete washout of biomass. In fact, the TSS equilibrated in all the second series reactors a value of around 400 mg/L. The VSS for the second series of reactors, likewise, decreased at the same rate as for the control and reached an equilibrium by the end of the study at around 300 mg/L. The percent of VSS in the second series of reactors remained fairly constant throughout the study. The control reactor, however, remained slightly higher than the waste-fed reactors indicating there may be some inorganic fraction that builds up in the second series of reactors.

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The purpose of the third series of reactors was to simulate the aerobic digesters at the Saxton POTW. After correcting for the fact that the control reactor possessed a higher initial concentration of solids after the restart of the test, the TSS in the waste-fed third series reactors was found to increase at the same rate as the control, but reached a lower equilibrium of about 2500 mg/L in the solvent-based waste-fed reactor and slightly less in the water-based waste-fed reactor or around 2200 mg/L. Likewise, the VSS of these reactors grew steadily and reached differing equilibriums towards the end of the study or around 2000 mg/L in the solvent-based waste-fed reactor and 1700 mg/L in the water-based waste-fed reactor. The percent VSS of these reactors resembled the control and remained somewhat constant throughout the study, but the water-based waste-fed reactor possessed a slightly lower value of 79 percent. This result indicates that there is an increase in the inorganic fraction that is becoming entrapped in the biomass and resulting sludge. The source of these solids is most likely the inorganic pigments used in the water-based wastes.

The TCOD of the mixed liquor in the first series of reactors showed little difference from the control while the second and third series of reactors showed no difference at all. The slight difference in the TCOD of the mixed liquor in reactor 7, the control, compared to the TCOD measured in reactors 1 and 4 may be due to failure of the control beyond day 15. This may be more easily seen in Figure 4.5.10 which shows a large peak in the SCOD in the period beyond day 15. Reactor 7 began to show signs of foaming which became progressively worse. It was first assumed that a surfactant may have contaminated the reactor, possibly originating from the detergent used to clean glassware in the laboratory. This assumption was discounted, however, as there was no indication of foaming in the second or third series of reactors (8 and 9) which receive their

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feed directly from reactor 7. If detergent had contaminated reactor 7 it would have contaminated each of the subsequent reactors. It was then assumed that the problem was biological, perhaps nutrient limited. Wet slides were made of the first series of reactors to assess any differences in the biomass cultures. Slides of each of the reactors contained examples of lightly loaded activated sludge floc with a multitude of bacteria species. Reactor 1 contained flagellates and ciliates including *Parameciums*, *Vorticella*, *Peranema*, *Chaenea*, and some unidentified filamentous bacteria. Reactor 4 possessed many more dispersed bacteria cells that were arranged in packets of two and four as well as many *Diplococcus* and *Sphaerotilus*. Also, present in reactor 4 were several examples of *Paramecium*. Reactor 7 appeared to possess a more dense floc with a marked difference in the amount of filamentous bacteria. There were many other bacteria within and around these filamentous strands. Bipolar protozoa were found in reactor 7, but few other examples of protozoa were observed. The NMB used in the feed solution contained a supply of nutrients, minerals and buffer. Additional buffer (1 ml) was added to each reactor daily as the pH dropped below 7.0 so that an abundant source of buffer was available. A review of the data obtained in the ammonia tests on day 15 showed a very low concentration in column 7. It was then assumed that nitrogen may have been the limiting factor. To test this idea, 5 ml of a 1 molar solution of ammonium chloride was added to reactor 7. As Figure 4.5.10 shows, the next series of SCOD tests showed a decrease. Towards the final days of the study some foam also began to appear in reactor 4 and finally in reactor 1. It was assumed that the ammonia content in the water-based waste being fed to reactor 1 may have been the reason foam took so long to develop in reactor 1. Another reason may have been the low amount of biological activity that occurred in reactors 1 through 6 during the failed first test. It is also important to note

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that the SCOD of the second series of reactors steadily remained below the residual COD value of 50 mg/L throughout the study even as the SCOD increased tremendously in the first series of reactors. This shows that a series operation of the activated sludge units works well to rough and polish the influent wastewaters.

A comparative analysis can be made of the GC data from the effluent wastewaters generated in reactors 1 through 6. Data in Figures 4.5.12, 4.5.13 and 4.5.14 indicate that solvents (mainly cyclohexanone) were present in the effluent of all the reactors. The only conclusion that can be made from the comparative analysis is that not all the compounds (solvents in particular) were degraded in both the series and parallel operation and within the aerobic digestion process. Additional quantitative gas chromatography and mass spectrophotometer (GC/MS) testing would be necessary to determine if the effluents meet effluent quality standards for hazardous waste discharge limits.

The results of respirometer tests on the effluent wastewaters on each of the bench-scale reactors (Figure 4.5.15) indicated a BOD of 1900 mg/L for the water-based waste-fed reactor and 1400 mg/L for the solvent-based waste-fed reactor. These high BOD values will exceed the POTW's permitted effluent BOD capacity. The respirometer tests further illustrated the benefit of a series operation as the BOD for the second series of reactors was significantly lower, or about 300 mg/L for the solvent-based waste-fed reactor and around 200 mg/L for the water-based waste-fed reactor. With a series operation the BOD rates could be lowered sufficiently to meet the POTW's permitted effluent BOD. The BOD indicated for the supernatant waters of the aerobic digesters was slightly higher, or around 700 mg/L, for both the solvent-based and water-based waste-fed reactors. This supernatant may place an added burden on the treatment process when

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rerouted back to the headworks of the POTW but could be managed through prudent operation of the existing equalization basins.

5.3 Pretreatment Methods

The Seton Company's Saxton Plant currently has the capability to alum-treat the wastewaters it generates. This treatment process is currently only used on the solvent-based wastewater. There is a significant reduction of BOD (85%) when alum treatment is used as is indicated by the aerobic respirometer results comparing the oxygen demand of booth 3 wastewater against the oxygen demand of the recycle wastewater (Figure 4.3.2). This reduction is due mainly to the removal of organic matter, but the low percentage of biodegradability shown in Table 5.1.1 indicates that a large amount of nonaerobically degradable organic matter remains solubilized in the wastewater even after treatment. This is confirmed in GC analysis in Figure 4.5.2. As indicated in Table 4.2.2, reductions of about 95 percent in SS loadings was evidenced in the treated solvent-based wastewater (booth 3 compared to recycle). Although a high percentage of SS was removed from the wastewater, the low percentage of biodegradability validates the assumption that a large amount of nonaerobically degradable organic matter remains solubilized in the wastewater after treatment. No samples of treated water-based samples were available for analysis or comparison. As the water-based wastewaters are high in SS and BOD, alum treatment could prove beneficial in their reduction. Also, as this study only investigated the aerobic treatability of the solvent-based and water-based wastewaters, no investigation was made into the possible beneficial effects of anaerobic treatability of these effluents. Further investigation should be made into other pretreatment methods available for the solvent-based and water-based wastewaters including microfiltration of the water-based wastewaters and solvent recovery by steam stripping, distillation or supercritical fluid

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extraction. Solvents recovered could be sold to pay for the cost of treatment. Recovery can be accomplished on-site or by commercial facilities costing about \$0.40 - \$1.55/gallon. The sell-back price is generally 80-90% of the virgin price of the compound (Breton, et al., 1988).

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Overall Conclusions

Preliminary findings using recirculated wastewaters and assuming a cumulative effect on concentration indicated that there would be only limited hydraulic impact on the Saxton POTW. Analysis showed that the optimum method of discharge from the Seton Company Saxton Plant would be a daily exchange of water in the booths. The expected increase in hydraulic flow would be 4500 gallons per day under current operations or 8000 gallons per day under future expanded operations. This equated to only 2 and 4 percent increases in average flow respectively. A daily exchange of water in the booths however, will result in a 30-fold increase in annual water use at the Seton Company.

Subsequent findings using nonrecirculated wastewaters proved the original assumption to be invalid as one-day samples possessed much higher concentrations than predicted. The differences in concentrations could be caused by the variability of chemicals and concentrations during the 36 day recirculation period, decay or volatility of measured parameters during the 36 day recirculation period, or by the fact that process waters at the time of one-day concentration sampling were unusually high. The overall effect to the Saxton POTW of a daily discharge using the nonrecirculated wastewater is an increase of 28% in average SS load under Seton's current operations and 54% under Seton's future operations. Even with this future increase in SS load, the treatment plant will be operating at only 51% of its design load capacity. The ammonia load on the treatment plant will increase 30% under Seton's current operations and 58% under Seton's future operations. The BOD load on the treatment plant will increase 90% under Seton's current operations and 172% under Seton's future operations. With the current Seton Company operations, the treatment plant will operate at 106% of its design BOD load capacity. With the Seton Company's future increase in BOD load, the treatment plant will

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operate at 151% of its design load capacity. From these results, complete discharge of all the Seton Company's wastewaters to the Saxton Wastewater Treatment Plant is not a viable option without some form of pretreatment to reduce the significant BOD load.

Aerobic respirometer tests indicate that all of the wastewater samples taken from the Seton Company's Saxton plant are aerobically biodegradable, but not to an extent that would make aerobic biological processes a viable sole option for the treatment of the leather finishing industry's effluent wastes. As only aerobic biological processes are currently available at the local Saxton POTW, the potential for sole aerobic treatment at the treatment facility is not a recommended option. Further investigation should be made on the advantages of anaerobic pretreatment of the wastewaters and effects of physical pretreatment on the biodegradability of the leather finishing industry's effluent wastes.

Bench-scale reactor tests indicated there was some additional suspended solids generated in the reactors fed with the solvent-based and water-based wastes. There was evidence, however that an inorganic fraction was building-up. This was more evident in the results of the second series of reactors in which the VSS for both of the waste-fed reactors was slightly higher than the control. Tests for SCOD also showed a toxic build-up, but results are questionable due to the failure of the control reactor toward the end of the test.

Comparative GC analysis of the effluents generated by the reactors showed the presence of solvents in both the water-based paints and solvent-based coatings. Further quantitative investigation should be made to determine whether the effluents meet effluent quality standards.

Final aerobic respirometer tests of the reactor effluents indicated that the first series of reactors (simulating parallel POTW operation) possessed BOD concentrations

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that were too high to meet the POTW's permitted effluent capacity. Tests on the second series of reactors (simulating series POTW operation) possessed significantly lower BOD values that would meet permitted effluent limits.

Overall, from the tests conducted in this study, the aerobic treatability of waste effluent from the leather finishing industry does show some promise. There is evidence that some of the many compounds used by the industry are aerobically degradable, but only to a limited extent. Complete treatment of the leather finishing effluents solely by the aerobic processes available at the Saxton POTW is not a viable option. Further investigation should be made into other forms of pretreatment including anaerobic treatment, microfiltration and solvent recovery.

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Appendix A

NUTRIENT MINERAL BUFFER MEDIUM FORMULATION

Nutrient Mineral Buffer Stock Solutions

1. Mineral Base I:

Add the following to 800 ml of reagent-quality water. Dilute to 1.0 liter. (Note: this mixture may form a light precipitate and should be agitated vigorously before transferring)

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	0.25 g	$\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$	0.005 g
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	2.0 g	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	0.025 g
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	0.05 g	Na_2SeO_4	0.025 g
H_3BO_3	0.025 g	CuCl_2	0.005 g
ZnCl_2	0.025 g		

2. Mineral Base II:

Add the following to 800 ml reagent-quality water. Dilute to 1.0 liter.

CaCl_2	15 g
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	20 g

3. Nutrient Base:

Add the following to 800 ml reagent-quality water. Adjust the pH to 7.0 with sodium hydroxide and dilute to 1.0 liter.

KH_2PO_4	50 g	Na_2SO_4	15 g
NH_4Cl	53 g		

4. Buffer Base:

Add the following to 800 ml distilled water. Dilute to 1.0 Liter.

KH_2PO_4	172 g
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Test Waste Feedstock Formulation

1. Add 1.0 ml each of Mineral Base I, Mineral Base II, and Nutrient Base to each liter of test waste to be used for testing.
2. Dilute with reagent-quality water to produce the desired test strength.

Appendix B

SAMPLE CALCULATIONS

Flows were determined using the fact that each booth possesses a 1000 gallon wastewater tank. It was assumed that an average cleanup volume of water was 500 gallons. For future expansion, the same rationale was used with the further assumption that twice as much cleanup water would be used, 1000 gallons. With this rationale it was determined that the flow rates to be expected would be 3500 gpd of water-based effluent under current operations:

Booth 1	1000 gallons
Booth 2	1000 gallons
Booth 4	1000 gallons
Cleanup	<u>500 gallons</u>
Total	3500 gallons

Under expanded operations, it was determined that the flow rates for water-based effluent would be 6000 gallons:

Booth 1	1000 gallons
Booth 2	1000 gallons
Booth 4	1000 gallons
Booth 5	1000 gallons
Booth 6	1000 gallons
Cleanup	<u>1000 gallons</u>
Total	6000 gallons

It was also determined that the flow rates to be expected would be 1000 gpd of solvent-based effluent under current operations:

Booth 3	<u>1000 gallons</u>
Total	1000 gallons

Under expanded operations, it was determined that the flow rates for solvent-based effluent would be 2000 gallons:

Booth 3	1000 gallons
Booth 7	<u>1000 gallons</u>
Total	2000 gallons

The suspended solids (SS) load was calculated using the total suspended solids (TSS) determined through laboratory analysis. The TSS of the holding tank sample was used to calculate the SS load for the water-based effluent as the holding tank is composed of wastewater from booths 1 and 2 as well as cleanup wastewater:

$$\text{Water-based Effluent SS Load} = [\text{TSS}_{(\text{holding tank})} \times \text{MGD} \times 8.34] = [40300 \times 0.0035 \times 8.34] = 1176 \text{ lb/day. Or for expanded operations, } [40300 \times 0.006 \times 8.34] = 2017 \text{ lb/day.}$$

The TSS of the booth 3 sample was used to calculate the SS load for the solvent-based effluent:

Appendix B

Solvent-based Effluent SS Load = $[TSS_{(Booth\ 3)} \times MGD \times 8.34] = [7800 \times 0.001 \times 8.34] = 65 \text{ lb/day}$. Or for expanded operations, $[7800 \times 0.002 \times 8.34] = 130 \text{ lb/day}$.

The TSS of the recycle sample was used to calculate the SS load for the solvent-based effluent after alum treatment:

Solvent-based Effluent SS Load with removal = $[TSS_{(Recycle)} \times MGD \times 8.34] = [370 \times 0.001 \times 8.34] = 3 \text{ lb/day}$. Or for expanded operations, $[370 \times 0.002 \times 8.34] = 6 \text{ lb/day}$.

The 5-day biochemical oxygen demand (BOD_5) load was calculated using 67% (theoretical value) of the ultimate BOD (BOD_U). The BOD_U was calculated using 50% (theoretical value) of the total chemical oxygen demand (TCOD) determined through laboratory analysis. The TCOD of the holding tank sample was used to calculate the BOD load for the water-based effluent as the holding tank is composed of wastewater from booths 1 and 2 as well as cleanup wastewater:

Water-based Effluent BOD Load = $[0.67 \times 0.5 \times TCOD_{(holding\ tank)} \times MGD \times 8.34] = [0.67 \times 0.5 \times 97500 \times 0.0035 \times 8.34] = 953 \text{ lb/day}$. Or for expanded operations, $[0.67 \times 0.5 \times 97500 \times 0.006 \times 8.34] = 1634 \text{ lb/day}$.

The TCOD of the booth 3 sample was used to calculate the BOD load for the solvent-based effluent:

Solvent-based Effluent BOD Load = $[0.67 \times 0.5 \times TCOD_{(Booth\ 3)} \times MGD \times 8.34] = [0.67 \times 0.5 \times 65000 \times 0.001 \times 8.34] = 182 \text{ lb/day}$. Or for expanded operations, $[0.67 \times 0.5 \times 65000 \times 0.002 \times 8.34] = 363 \text{ lb/day}$.

The TCOD of the recycle sample was used to calculate the BOD load for the solvent-based effluent after alum treatment:

Solvent-based Effluent BOD Load with Removal = $[0.67 \times 0.5 \times TCOD_{(Recycle)} \times MGD \times 8.34] = [0.67 \times 0.5 \times 10500 \times 0.001 \times 8.34] = 29 \text{ lb/day}$. Or for expanded operations, $[0.67 \times 0.5 \times 10500 \times 0.002 \times 8.34] = 59 \text{ lb/day}$.

The ammonia-nitrogen (NH_3-N) load was calculated using the NH_3-N concentrations determined through laboratory analysis. The NH_3-N of the holding tank sample was used to calculate the NH_3-N load for the water-based effluent as the holding tank is composed of wastewater from booths 1 and 2 as well as cleanup wastewater:

Water-based Effluent NH_3-N Load = $[NH_3-N_{(holding\ tank)} \times MGD \times 8.34] = [760 \times 0.0035 \times 8.34] = 22 \text{ lb/day}$. Or for expanded operations, $[760 \times 0.006 \times 8.34] = 38 \text{ lb/day}$.

The NH_3-N of the booth 3 sample was used to calculate the NH_3-N load for the solvent-based effluent:

Appendix B

Solvent-based Effluent $\text{NH}_3\text{-N}$ Load = $[\text{NH}_3\text{-N}_{(\text{Booth 3})} \times \text{MGD} \times 8.34] = [3920 \times 0.001 \times 8.34] = 33 \text{ lb/day}$. Or for expanded operations, $[3920 \times 0.002 \times 8.34] = 65 \text{ lb/day}$.

The $\text{NH}_3\text{-N}$ of the recycle sample was used to calculate the $\text{NH}_3\text{-N}$ load for the solvent-based effluent after alum treatment:

Solvent-based Effluent $\text{NH}_3\text{-N}$ Load with Removal = $[\text{NH}_3\text{-N}_{(\text{Recycle})} \times \text{MGD} \times 8.34] = [298 \times 0.001 \times 8.34] = 2 \text{ lb/day}$. Or for expanded operations, $[298 \times 0.002 \times 8.34] = 5 \text{ lb/day}$.

The estimated sludge load was calculated assuming 50 percent of the SS load, 40 percent of the BOD load and 20 percent of the ammonia nitrogen load will go directly to sludge:

Water-based Effluent Sludge Load = $[0.5 \times \text{SS load} \times 0.4 \times \text{BOD load} \times 0.2 \times \text{NH}_3\text{-N load}] = [0.5 \times 1176 \times 0.4 \times 953 \times 0.2 \times 22] = 974 \text{ lb/day}$. Or for expanded operations, $[0.5 \times 2017 \times 0.4 \times 1634 \times 0.2 \times 38] = 1670 \text{ lb/day}$.

Solvent-based Effluent Sludge Load = $[0.5 \times \text{SS load} \times 0.4 \times \text{BOD load} \times 0.2 \times \text{NH}_3\text{-N load}] = [0.5 \times 65 \times 0.4 \times 182 \times 0.2 \times 33] = 112 \text{ lb/day}$. Or for expanded operations, $[0.5 \times 130 \times 0.4 \times 363 \times 0.2 \times 65] = 223 \text{ lb/day}$.

Solvent-based Effluent Sludge Load with Removal = $[0.5 \times \text{SS load} \times 0.4 \times \text{BOD load} \times 0.2 \times \text{NH}_3\text{-N load}] = [0.5 \times 3 \times 0.4 \times 29 \times 0.2 \times 2] = 14 \text{ lb/day}$. Or for expanded operations, $[0.5 \times 6 \times 0.4 \times 59 \times 0.2 \times 5] = 28 \text{ lb/day}$.

Appendix C

Bench-scale Reactor Feedstock Determinations

The purpose of the bench-scale reactors was to simulate the Saxton POTW treatment process. As such, it was decided that the amount of waste fed to the reactors would be proportional in volume to that which would be received at the POTW. The waste feed stock was prepared by blending process waters of booths 1, 2, and 4 in equal parts then adding equivalent half part of cleanup water (1:1:1:0.5) to make up the stock water-based feed. The stock solvent-based feed was merely process water from booth 3. Ratios were then established for each wastewater assuming the volumes the Seton Company is currently generating. Ethanol was used as a control substrate. A feed volume had to be determined to maintain a 1 g COD/L/day feed loading.

Control Feedstock:

Assuming 1.0 mL of ethanol = 1.67 g COD,

$$6 \text{ mL/L/day} = 10.02 \text{ g COD/10 L/day} = 1 \text{ g COD/L/day}$$

So, 6 mL of ethanol was diluted to one liter (10 day SRT) with NMB and fed to reactor 7 daily.

Water-based wastes (WBW):

$$3500 \text{ gallons WBW/200,000 gallons Design Average Flow (DAF)} = 0.0175\%$$

So, for every liter of wastewater entering the POTW, 0.0175 liters or 17.5 ml will be Seton Company water-based process water. The COD of this wastewater was then determined using the TCOD measured:

$$[19950 \text{ mg COD/L}]/[1000 \text{ mL/L}] = [19.95 \text{ mg COD/mL}]/[1000 \text{ mg/g}] = 0.01995 \text{ gCOD}$$

$$17.5 \text{ mL/L/day} = 0.35 \text{ g COD/10 L/day} = 0.035 \text{ g COD/L/day}$$

Since this proportion of Seton Company wastes possesses such a small amount of COD and a 1 g COD/L/day loading rate was desired, the remaining COD load was made up

Appendix C

with ethanol. Thus, 6 mL of ethanol and 17.5 ml of water-based wastes was diluted with NMB to one liter (10 day SRT) and added to reactor 1 daily.

Solvent-based wastes (SBW):

$$1000 \text{ gallons SBW}/200,000 \text{ gallons DAF at POTW} = 0.005\%$$

So, for every liter of wastewater entering the POTW, 0.005 liters or 5 ml will be Seton Company solvent-based process water. The COD of this wastewater was then determined using the TCOD measured:

$$[35750 \text{ mg COD/L}]/[1000 \text{ mL/L}] = [35.75 \text{ mg COD/mL}]/[1000 \text{ mg/g}] = 0.03575 \text{ gCOD}$$

$$5 \text{ mL/L/day} = 0.18 \text{ g COD}/10 \text{ L/day} = 0.018 \text{ g COD/L/day}$$

Since this proportion of Seton Company wastes possesses such a small amount of COD and a 1 g COD/L/day loading rate was desired, the remaining COD load was made up with ethanol. Thus, 6 mL of ethanol and 5 ml of water-based wastes was diluted with NMB to one liter (10 day SRT) and added to reactor 4 daily.

Reactor 10 Feedstock:

The feedstock for reactor 10 was determined in a similiar manner except that the reactor volume was only 8 liters. Since this reactor was to simulate a mixed feed of solvent and water-based wastes, a ratio was set up using their combined proportional flows:

$$4500 \text{ gallons}/200,000 \text{ gallons DAF at POTW} = 0.0225\%$$

So, for every liter of wastewater entering the POTW, 0.0225 liters or 22.5 ml will be Seton Company solvent-based process water (17.5 ml WBW and 5 ml SBW). The wastewater's COD was then determined using the TCOD measured for each waste and adding.

For water-based:

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$$[19950 \text{ mg COD/L}]/[1000 \text{ mL/L}] = [19.95 \text{ mg COD/mL}]/[1000 \text{ mg/g}] = 0.01995 \text{ gCOD}$$

$$17.5 \text{ mL/L/day} = 0.35 \text{ g COD/8 L/day} = 0.0438 \text{ g COD/L/day}$$

For solvent-based:

$$[35750 \text{ mg COD/L}]/[1000 \text{ mL/L}] = [35.75 \text{ mg COD/mL}]/[1000 \text{ mg/g}] = 0.03575 \text{ gCOD}$$

$$5 \text{ mL/L/day} = 0.18 \text{ g COD/8 L/day} = 0.0225 \text{ g COD/L/day}$$

For combined Waste:

$$0.0438 \text{ g COD/L/day} + 0.0225 \text{ g COD/L/day} = 0.0663 \text{ g COD/L/day}$$

Since this proportion of Seton Company wastes possesses such a small amount of COD and a 1 g COD/L/day loading rate was also desired for this reactor, the remaining COD load was made up with ethanol. Again, assuming 1.0 mL of ethanol = 1.67 g COD,

$$4.8 \text{ mL/L/day} = 8.02 \text{ g COD/8 L/day} = 1 \text{ g COD/L/day}$$

Thus, 4.8 mL of ethanol and 5 ml of water-based wastes was diluted with NMB to 1.6 liter (5 day SRT) and added to reactor 10 daily.

Appendix D

BENCH-SCALE REACTOR DATA

7/10/83 Day 1										7/12/83 Day 3									
PAN#	WT	corrected	106	660	Vp	TSS	AVG	STD DEV	VSS	AVG	STD DEV	VSS	AVG	STD DEV	VSS	AVG	STD DEV	VSS	Percent
1/1	0.1280	0.1266	0.1434	0.1265	25	672	648	24	556	544	12	84	544	12	84	544	12	84	
1/2	0.1280	0.1266	0.1422	0.1269	25	624	648	24	532	544	12	84	544	12	84	544	12	84	
2/1	0.1265	0.1241	0.1412	0.1268	25	684	678	6	576	568	8	84	568	8	84	568	8	84	
2/2	0.1246	0.1232	0.1400	0.1260	25	672	678	6	560	568	8	84	568	8	84	568	8	84	
3/1	0.1258	0.1244	0.1405	0.1266	25	644	668	24	556	570	14	85	570	14	85	570	14	85	
3/2	0.1274	0.1260	0.1433	0.1267	25	682	668	24	584	570	14	85	570	14	85	570	14	85	
4/1	0.1253	0.1239	0.1411	0.1263	25	688	672	16	592	580	12	86	580	12	86	580	12	86	
4/2	0.1279	0.1265	0.1429	0.1267	25	656	672	16	568	580	12	86	580	12	86	580	12	86	
5/1	0.1271	0.1257	0.1420	0.1276	25	652	652	0	576	572	4	86	572	4	86	572	4	86	
5/2	0.1274	0.1260	0.1423	0.1281	25	652	652	0	568	572	4	86	572	4	86	572	4	86	
6/1	0.1265	0.1251	0.1414	0.1273	25	652	650	2	564	560	4	86	560	4	86	560	4	86	
6/2	0.1242	0.1228	0.1390	0.1251	25	648	650	2	556	560	4	86	560	4	86	560	4	86	
7/1	0.1252	0.1238	0.1519	0.1275	25	1124	1134	10	976	966	10	87	966	10	87	966	10	87	
7/2	0.1269	0.1255	0.1541	0.1292	25	1144	1134	10	988	966	10	87	966	10	87	966	10	87	
8/1	0.1259	0.1245	0.1532	0.1282	25	1148	1122	26	1000	976	24	87	976	24	87	976	24	87	
8/2	0.1264	0.1250	0.1524	0.1286	25	1088	1122	26	952	976	24	87	976	24	87	976	24	87	
9/1	0.1247	0.1233	0.1525	0.1272	25	1168	1110	58	1012	956	56	86	956	56	86	956	56	86	
9/2	0.1263	0.1249	0.1512	0.1267	25	1052	1110	58	900	956	56	86	956	56	86	956	56	86	
7/12/83 Day 3										7/12/83 Day 3									
PAN#	WT	corrected	106	660	Vp	TSS	AVG	STD DEV	VSS	AVG	STD DEV	VSS	AVG	STD DEV	VSS	AVG	STD DEV	VSS	Percent
1/1	0.1246	0.1231	0.1466	0.1266	25	940	968	26	800	820	20	85	820	20	85	820	20	85	
1/2	0.1273	0.1259	0.1507	0.1267	25	962	968	26	840	820	20	85	820	20	85	820	20	85	
2/1	0.1261	0.1247	0.1407	0.1273	25	640	632	8	536	534	2	84	534	2	84	534	2	84	
2/2	0.1266	0.1252	0.1408	0.1275	25	624	632	8	532	534	2	84	534	2	84	534	2	84	
3/1	0.1248	0.1234	0.1439	0.1270	25	820	632	8	676	534	2	84	534	2	84	534	2	84	
3/2	0.1252	0.1238	0.1432	0.1273	25	776	796	22	636	656	20	82	656	20	82	656	20	82	
4/1	0.1255	0.1241	0.1581	0.1302	25	1360	796	22	1116	656	20	82	656	20	82	656	20	82	
4/2	0.1253	0.1239	0.1501	0.1265	25	1048	1204	156	864	980	126	82	980	126	82	980	126	82	
5/1	0.1284	0.1260	0.1432	0.1304	25	608	1204	156	512	980	126	82	980	126	82	980	126	82	
5/2	0.1262	0.1248	0.1400	0.1273	25	608	608	0	508	510	2	84	510	2	84	510	2	84	
6/1	0.1268	0.1254	0.1460	0.1294	25	824	608	0	664	510	2	84	510	2	84	510	2	84	
6/2	0.1253	0.1239	0.1436	0.1275	25	788	608	18	644	510	2	84	510	2	84	510	2	84	
7/1	0.1254	0.1240	0.1550	0.1278	25	1240	608	18	1088	654	10	81	654	10	81	654	10	81	
7/2	0.1276	0.1262	0.1562	0.1300	25	1200	1220	20	1088	1088	20	88	1088	20	88	1088	20	88	
8/1	0.1252	0.1238	0.1464	0.1275	25	1024	1220	20	876	1088	20	88	1088	20	88	1088	20	88	
8/2	0.1252	0.1238	0.1461	0.1276	25	972	996	26	876	1088	20	88	1088	20	88	1088	20	88	
9/1	0.1265	0.1251	0.1600	0.1325	25	1316	996	26	1100	846	26	85	846	26	85	846	26	85	
9/2	0.1239	0.1225	0.1537	0.1274	25	1248	1282	34	1052	1076	24	84	1076	24	84	1076	24	84	

Appendix D

7/14/93 Day 5	WT	corrected	106	646	Vp	TSS	AVG	STD DEV	VSS	AVG	STD DEV	Percent
PAN#												
1/1	0.1276	0.1262	0.1522	0.1295	25	1040	1028	12	908	900	8	88
1/2	0.1285	0.1271	0.1525	0.1302	25	1016			892			
2/1	0.1265	0.1251	0.1395	0.1296	25	536	546	10	464	472	8	86
2/2	0.1247	0.1233	0.1372	0.1252	25	556			480			
3/1	0.1250	0.1236	0.1468	0.1274	25	928	932	4	776	776	0	83
3/2	0.1251	0.1237	0.1471	0.1277	25	936			920			
4/1	0.1286	0.1262	0.1539	0.1309	25	1028	1028	0	924	922	2	90
4/2	0.1264	0.1270	0.1527	0.1296	25	524			440			
5/1	0.1266	0.1272	0.1403	0.1293	25	528	526	2	440	440	0	84
5/2	0.1278	0.1264	0.1396	0.1286	25	904			760			
6/1	0.1260	0.1246	0.1472	0.1282	25	876	860	14	740	750	10	84
6/2	0.1258	0.1244	0.1463	0.1276	25	1304			1176			
7/1	0.1260	0.1266	0.1592	0.1296	25	1316	1310	6	1196	1186	10	91
7/2	0.1260	0.1266	0.1595	0.1296	25	796			688			
8/1	0.1267	0.1273	0.1472	0.1300	25	766	782	14	688	678	10	87
8/2	0.1255	0.1241	0.1433	0.1286	25	1360			1188			
9/1	0.1246	0.1234	0.1579	0.1282	25	1448	1414	34	1228	1206	20	85
9/2	0.1274	0.1260	0.1622	0.1315	25							

7/16/93 Day 7	WT	corrected	106	646	Vp	TSS	AVG	STD DEV	VSS	AVG	STD DEV	Percent
PAN#												
1/1	0.1273	0.1259	0.1569	0.1303	25	1240	1214	26	1084	1054	10	87
1/2	0.1261	0.1247	0.1544	0.1283	25	1168			1044			
2/1	0.1234	0.1220	0.1350	0.1245	25	520	524	4	420	420	0	80
2/2	0.1239	0.1225	0.1357	0.1252	25	528			900			
3/1	0.1229	0.1215	0.1492	0.1267	25	1108	1110	2	908	904	4	81
3/2	0.1237	0.1223	0.1501	0.1274	25	1112			1112			
4/1	0.1272	0.1258	0.1570	0.1292	25	1248	1184	64	1004	1058	54	89
4/2	0.1251	0.1237	0.1517	0.1266	25	1120			390			
5/1	0.1251	0.1237	0.1353	0.1258	25	464	470	6	398	394	4	82
5/2	0.1256	0.1242	0.1361	0.1264	25	476			864			
6/1	0.1228	0.1214	0.1467	0.1271	25	1092	1074	18	864	854	10	80
6/2	0.1244	0.1230	0.1464	0.1283	25	1056			1312			
7/1	0.1249	0.1235	0.1600	0.1272	25	1460	1394	66	1196	1254	58	90
7/2	0.1241	0.1227	0.1559	0.1260	25	1328			564			
8/1	0.1214	0.1200	0.1373	0.1232	25	692	686	6	564	564	0	82
8/2	0.1251	0.1237	0.1407	0.1286	25	680			1346			
9/1	0.1251	0.1241	0.1644	0.1307	25	1612	1636	24	1396	1372	24	84
9/2	0.1255	0.1241	0.1644	0.1307	25	1600						
9/2	0.1223	0.1209	0.1624	0.1275	25							

Appendix D

7/22/83 Day 13		WT		corrected		106		660		Vp		TSS		AVG		STD DEV		VSS		AVG		STD DEV		Percent	
PAN#																									
10/1	0.1268	0.1268	0.1254	0.1254	0.1403	0.1268	15	983	1507	15	983	1507	1507	930	1517	10	1363	1353	847	53	91				
10/2	0.1274	0.1274	0.1260	0.1260	0.1390	0.1271	15	987	1527	15	987	1527	1527		463	10	347	1373							
									473	15		473			1680	93	347	1373							
									453	15		453			1337	80	347	1373							
									1773	15		1773			1187	89	1400	1373							
									1587	15		1587			1190	3	1400	1373							
									1333	15		1333			323	3	1400	1373							
									447	15		447			1307	20	1400	1373							
									420	15		420			432	12	1400	1373							
									1680	15		1680			408	82	1400	1373							
									1533	15		1533			1713	82	1400	1373							
									1400	15		1400			1720	3	1400	1373							
									1467	15		1467			967	0	1400	1373							
									520	25		520			967	0	1400	1373							
									504	25		504			967	0	1400	1373							
									2080	15		2080			967	0	1400	1373							
									2107	15		2107			967	0	1400	1373							
									1107	15		1107			967	0	1400	1373							
									1107	15		1107			967	0	1400	1373							
									1107	15		1107			967	0	1400	1373							
									1107	15		1107			967	0	1400	1373							
									1107	15		1107			967	0	1400	1373							
									1107	15		1107			967	0	1400	1373							
									1107	15		1107			967	0	1400	1373							
									1107	15		1107			967	0	1400	1373							
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									1107	15		1107			967	0	1400	1373							
									1107	15		1107			967	0	1400	1373							
									1107	15		1107			967	0	1400	1373							
									1107	15		1107			967	0	1400	1373							
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									1107	15		1107			967	0	1400	1373							
									1107	15		1107			967	0	1400	1373							
									1107	15		1107			967										

Appendix D

8/2	0.1283	0.1279	0.1355	0.1292	15	507	487	10	420	427	7	86
9/1	0.1259	0.1245	0.1579	0.1300	15	2227	2193	33	1860	1837	23	84
9/2	0.1258	0.1244	0.1568	0.1296	15	2160	2183	33	1813	1837	23	84
10/1	0.1285	0.1271	0.1433	0.1287	15	1080	1083	3	973	983	10	91
10/2	0.1273	0.1259	0.1422	0.1273	15	1087	1083	3	983	983	10	91
9/1	0.1213	0.1199	0.1362	0.1215	15	1067	1050	37	980	980	150	79
9/2	0.1230	0.1216	0.1368	0.1266	15	1013	1050	37	680	830	150	79

7/29/83 Day 20	WT	corrected	106	660	Vp	TSS	AVG	STD DEV	VSS	AVG	STD DEV	Percent
PAN#												
1/1	0.1286	0.1282	0.1453	0.1300	10	1710	1615	95	1530	1440	90	89
1/2	0.1272	0.1258	0.1410	0.1275	10	1520	1615	95	1350	1440	90	89
2/1	0.1263	0.1249	0.1331	0.1265	25	328	328	0	284	270	6	82
2/2	0.1238	0.1224	0.1308	0.1237	25	328	328	0	276	270	6	82
3/1	0.1298	0.1284	0.1498	0.1325	10	2140	2070	70	1730	1675	55	81
3/2	0.1280	0.1246	0.1446	0.1284	10	2000	2070	70	1620	1675	55	81
4/1	0.1269	0.1255	0.1398	0.1270	10	1410	1375	35	1260	1225	35	89
4/2	0.1284	0.1270	0.1404	0.1285	10	1340	1375	35	1190	1225	35	89
5/1	0.1289	0.1275	0.1357	0.1298	25	328	320	8	244	238	6	74
5/2	0.1246	0.1232	0.1310	0.1252	25	312	320	8	232	238	6	74
6/1	0.1241	0.1227	0.1433	0.1284	10	2060	2055	5	1690	1690	10	82
6/2	0.1228	0.1214	0.1419	0.1252	10	2050	2055	5	1670	1690	10	82
7/1	0.1268	0.1252	0.1371	0.1280	10	1190	1215	25	1110	1115	5	92
7/2	0.1261	0.1247	0.1371	0.1259	10	1240	1215	25	1120	1115	5	92
8/1	0.1265	0.1251	0.1339	0.1267	25	352	358	6	288	284	6	82
8/2	0.1268	0.1254	0.1345	0.1270	25	364	358	6	300	284	6	82
9/1	0.1224	0.1210	0.1461	0.1241	10	2510	2525	15	2200	2180	40	86
9/2	0.1253	0.1239	0.1463	0.1261	10	2540	2525	15	2120	2180	40	86
10/1	0.1254	0.1240	0.1353	0.1258	10	1130	1135	5	950	930	20	82
10/2	0.1266	0.1252	0.1366	0.1275	10	1140	1135	5	910	930	20	82
9/1	0.1242	0.1228	0.1310	0.1244	10	820	835	15	660	685	25	82
9/2	0.1282	0.1278	0.1363	0.1292	10	850	835	15	710	685	25	82

8/03/83 Day 25	WT	corrected	106	660	Vp	TSS	AVG	STD DEV	VSS	AVG	STD DEV	Percent
PAN#												
1/1	0.1300	0.1286	0.1467	0.1309	10	2010	1940	70	1780	1705	75	88
1/2	0.1244	0.1230	0.1417	0.1254	10	1870	1940	70	1630	1705	75	88
2/1	0.1236	0.1222	0.1324	0.1242	25	408	414	6	328	330	2	80
2/2	0.1246	0.1232	0.1337	0.1254	25	420	414	6	332	330	2	80
3/1	0.1250	0.1236	0.1466	0.1261	10	2300	2275	25	1850	1835	15	81
3/2	0.1232	0.1218	0.1443	0.1261	10	2250	2275	25	1820	1835	15	81
4/1	0.1265	0.1251	0.1444	0.1272	10	1930	2275	25	1720	1835	15	81

Appendix D

8/09/93 Day 30													
PAN#	WT	corrected	106	680	Vp	TSS	AVG	STD DEV	VSS	AVG	STD DEV	0	90
4/2	0.1240	0.1226	0.1416	0.1244	10	1900	1915	15	1720	1720	0	90	
5/1	0.1312	0.1298	0.1376	0.1315	25	312	308	4	244	244	0	79	
5/2	0.1256	0.1242	0.1318	0.1257	25	304	308	4	244	244	0	79	
6/1	0.1301	0.1287	0.1525	0.1333	10	2380	2400	20	1920	1920	20	81	
6/2	0.1265	0.1251	0.1493	0.1297	10	2420	2400	20	1960	1940	20	81	
7/1	0.1275	0.1261	0.1420	0.1276	10	1590	1685	95	1440	1510	70	90	
7/2	0.1280	0.1266	0.1355	0.1276	5	1780	1685	95	1580	1510	70	90	
8/1	0.1239	0.1225	0.1324	0.1239	25	398	392	4	340	328	12	84	
8/2	0.1279	0.1265	0.1362	0.1263	25	388	392	4	316	328	12	84	
9/1	0.1256	0.1242	0.1494	0.1266	10	2520	2595	75	2080	2165	85	83	
9/2	0.1266	0.1252	0.1519	0.1264	10	2670	2595	75	2250	2165	85	83	
10/1	0.1270	0.1256	0.1328	0.1265	5	1440	1510	70	1260	1310	50	87	
10/2	0.1282	0.1278	0.1357	0.1269	5	1580	1510	70	1360	1310	50	87	
9/1	0.1221	0.1207	0.1318	0.1223	10	1110	1110	0	960	955	5	86	
9/2	0.1226	0.1212	0.1323	0.1227	10	1110	1110	0	960	955	5	86	
9/1a	0.1201	0.1187	0.1304	0.1216	10	1170	1150	20	880	865	15	75	
9/2a	0.1203	0.1189	0.1302	0.1217	10	1130	1150	20	850	865	15	75	
8/09/93 Day 30													
PAN#	WT	corrected	106	680	Vp	TSS	AVG	STD DEV	VSS	AVG	STD DEV	Percent	
1/1	0.1267	0.1253	0.1454	0.1277	10	2010	2055	45	1770	1805	35	88	
1/2	0.1246	0.1232	0.1337	0.1245	5	2100	2055	45	1840	1805	35	88	
2/1	0.1305	0.1291	0.1389	0.1309	25	392	394	2	320	322	2	82	
2/2	0.1241	0.1227	0.1326	0.1245	25	396	394	2	324	322	2	82	
3/1	0.1263	0.1249	0.1477	0.1300	10	2280	2280	10	1770	1780	10	78	
3/2	0.1272	0.1258	0.1488	0.1309	10	2300	2280	10	1790	1780	10	78	
4/1	0.1236	0.1222	0.1428	0.1243	10	2060	1985	65	1850	1790	60	90	
4/2	0.1259	0.1245	0.1438	0.1265	10	1930	1985	65	1730	1790	60	90	
5/1	0.1256	0.1242	0.1334	0.1260	25	368	362	6	296	298	2	82	
5/2	0.1316	0.1302	0.1391	0.1316	25	356	362	6	300	298	2	82	
6/1	0.1296	0.1282	0.1529	0.1327	10	2470	2490	20	2020	2040	20	82	
6/2	0.1309	0.1295	0.1546	0.1340	10	2510	2490	20	2060	2040	20	82	
7/1	0.1269	0.1255	0.1344	0.1264	5	1780	1780	0	1600	1600	0	90	
7/2	0.1264	0.1250	0.1339	0.1259	5	1780	1780	0	1600	1600	0	90	
8/1	0.1255	0.1241	0.1334	0.1253	25	372	372	0	324	316	8	85	
8/2	0.1233	0.1219	0.1312	0.1235	25	372	372	0	308	316	8	85	
9/1	0.1262	0.1248	0.1509	0.1290	10	2610	2660	50	2190	2220	30	83	
9/2	0.1272	0.1258	0.1529	0.1304	10	2710	2660	50	2250	2220	30	83	
10/1	0.1260	0.1246	0.1582	0.1282	25	1344	1362	38	1200	1225	25	89	
10/2	0.1266	0.1252	0.1394	0.1269	10	1420	1362	38	1250	1225	25	89	

8/09/03 Day 30

Appendix D

Reactor Summary TSS											
Day	Reactor	1	2	3	4	5	6	7	8	9	10
1		948	678	668	672	651	650	1134	1122	1110	978
3		906	632	798	1204	608	806	1220	998	1282	930
5		1028	546	932	1028	528	890	1310	782	1414	1107
7		1214	524	1110	1184	470	1074	1394	686	1636	1083
9		1238	504	1316	1112	442	1242	1384	654	1792	1120
11		1297	427	1513	1290	397	1393	1493	627	1920	835
13		1517	463	1680	1343	433	1607	1433	512	2093	1130
15		1297	357	1750	1280	347	1737	1303	497	2193	1150
20		1615	328	2070	1375	320	2055	1215	358	2525	1382
25		1940	414	2275	1915	308	2400	1685	392	2595	
30		2055	394	2280	1995	362	2460	1780	372	2680	
Reactor Summary VSS											
Day	Reactor	1	2	3	4	5	6	7	8	9	10
1		544	568	570	580	572	560	986	976	956	844
3		820	534	656	990	510	654	1068	848	1076	847
5		900	472	776	922	440	750	1186	678	1208	967
7		1054	420	904	1058	394	854	1254	564	1372	983
9		1100	406	1066	990	350	998	1262	556	1500	990
11		1181	370	1253	1203	330	1160	1413	580	1647	685
13		1363	347	1337	1190	323	1310	1307	420	1717	1020
15		1177	260	1443	1163	295	1410	1193	427	1837	865
20		1440	270	1675	1225	238	1680	1115	294	2180	1225
25		1705	330	1835	1720	244	1940	1510	328	2165	
30		1805	322	1780	1790	298	2040	1600	316	2220	
Reactor Summary Percent VSS											
Day	Reactor	1	2	3	4	5	6	7	8	9	10
1		84	84	85	86	88	86	87	87	86	86
3		85	84	82	82	84	81	88	85	84	81
5		86	86	83	90	84	84	91	87	85	87
7		87	80	81	89	82	80	90	82	84	91
9		89	81	81	89	79	80	91	85	84	88
11		91	87	83	93	85	83	95	89	86	82
13		90	75	80	89	75	82	91	82	82	90
15		91	73	82	92	85	81	92	86	84	75
20		89	82	81	89	74	82	92	82	86	89
25		88	80	81	90	79	81	90	84	83	
30		88	82	78	90	82	82	90	85	83	

Appendix D

TCOD Day	Reactor	1	2	3	4	5	6	7	8	9	10
1	1	950	980	988	891	885	882	1330	1342	1241	1383
3	3	1251	770	977	1191	728	981	1535	1138	1539	2165
5	5	1382	686	1136	1318	612	1080	1680	952	1786	1671
7	7	1820	607	1393	1542	528	1308	1650	853	1910	1762
9	9	1598	574	1586	1446	471	1462	1844	712	2206	1698
11	11	1687	454	1603	1504	393	1580	1878	835	2305	1303
13	13	1905	438	1770	1685	405	1806	1802	567	2573	1442
15	15	1780	389	1980	1656	397	1910	1718	508	2622	1514
20	20	1901	382	2446	1814	328	2192	1598	420	2747	1858
25	25	2134	436	2367	2257	302	2343	1783	386	2854	1869
30	30	2326	436	2420	2146	387	2484	1908	400	2712	2641

SCOD Day	Reactor	1	2	3	4	5	6	7	8	9	10
1	1	206	190	191	133	158	141	53	79	68	116
3	3	84	35	46	53	36	43	47	46	38	805
5	5	90	34	29	51	21	25	28	32	35	155
7	7	90	34	33	64	27	35	32	29	32	176
9	9	75	39	37	81	38	42	40	34	47	239
11	11	66	30	27	83	27	24	37	13	21	280
13	13	104	37	29	93	33	43	59	32	37	272
15	15	100	42	49	149	42	48	80	25	37	389
20	20	144	39	38	210	38	38	172	24	25	315
25	25	147	48	53	189	37	46	302	25	39	768
30	30	277	56	64	211	43	52	176	30	45	1353